

## **Part 2 - Session Papers for the EPA 22<sup>nd</sup> Annual National Conference on Managing Environmental Quality Systems**

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\* **Abstract Only**

# **Standard Operating Procedure 2002-1 on Product Properties Data Requirements for Registration and Reregistration of Pesticides**

<sup>1/</sup>Sami Malak and Betsy Grim

<sup>1/</sup>OPP's QA Officer: Phone: 703-308-9365, e-mail: malak.sami@epa.gov  
Office of Pesticide Programs (7505C), 1200 Pennsylvania Ave, NW,  
Washington, DC 20460-0001

## **INTRODUCTION:**

The need for a Standard Operating Procedure (SOP) on product properties data requirements for registration and reregistration of pesticides was recognized following the 1997 reorganization of the Office of Pesticide Programs (OPP) of the Environmental Protection Agency (EPA) and assigning the review and decision-making process to four OPP's divisions, which are: Registration Division (RD), Antimicrobials Division (AD), Special Review and Reregistration Division (SRRD), and Health Effects Division (HED). This need was outlined in OPP's Quality Assurance Annual Report and Work Plan (QAARWP) for a period of three years and was given a top priority by an auditing team from the Office of Environmental Information (OEI). The team was briefed on certain weaknesses in pesticide properties data submitted by registrants/applicants seeking registration or reregistration of pesticides. These weaknesses are attributed to: (a) certain caveats in the regulations; and (b) inconsistencies among the science and regulatory divisions in OPP engaged in reviewing product properties. Consequently, OPP's Quality Assurance (QA) manager and officers were directed to write a SOP for the purpose of harmonizing scientific and regulatory issues among OPP's divisions and project, with explanations, any noted caveats.

OPPTS Test Guidelines, Series 830, Product Properties [6], is a harmonized guidelines with the Organization for Economic Cooperation and Development (OECD). However, it contains certain caveats identified in a recent publication [11] cited in the SOP. The 89 pages SOP is a comprehensive document that covers all aspects of product properties and distills the expertise of OPP's scientists and QA officers across all disciplines. It is anticipated that it will provide adequate guidance to reviewers of product properties for the purpose of harmonizing the review and decision making-process by the Agency.

## **I. DIRECTIVE TOPICS IN THE STANDARD OPERATING PROCEDURE**

### **1. Purpose of the SOP**

(a) To give directions to reviewers of product properties in the Office of Pesticide Programs' Divisions: RD, AD, SRRD, and HED; (b) To achieve harmonization and consistency in the review and decision-making process by the Agency; (c) To explain certain caveats and non-specificity in OPPTS Test Guidelines, Series 830, Product Properties [6]; and (d) To encourage registrants/applicants to submit quality data for advancing the quality of reviews and decisions.

## 2. Definitions of Certain Terms

- (a) Product Properties: Is the science that elucidates the chemistry, identity, composition, analysis and properties of pesticide products. Pesticides can be classified into two major categories: conventional, including antimicrobials; and biopesticides, which include biochemical pesticides, microbial pesticides, and plant-incorporated protectants (PIPs).
- (b) Non-Integrated Products: Manufacturing-Use (MP) and End-Use (EP) pesticide products formulated using registered sources with no intended chemical reaction. This definition and the specific data requirements are stipulated in Pesticide Registration (PR) Notice 98-1 on self-certification of product properties data [9].
- (c) Integrated products: All Products other than non-integrated.
- (d) Nominal Concentration: The percent of a pure ingredient within the minimum and maximum guarantee that is most likely to be present in a typical sample of a pesticide product as determined by validated analytical techniques from production to use.

Explanations to the above definitions: Definition (a) has never been defined in the regulations. Definition (b) allows only registered sources to be used in the formulation, a specific term that has never been used in the regulations. Definition (c) covers formulated products as well as manufactured, a term that is overlooked in the regulations (Table III). Definition (d) currently defined erroneously in the regulations as “the percentage by weight”, a reason for the high rejection rate in the reviews of product properties attributed to errors in expressing the nominal concentration of pesticides in the Confidential Statements of Formula (CSF) and inconsistency between the label and CSF in citing the ingredient statement (please refer to a recent publication [11] for detailed discussion that projected this definition).

## 3. Who Is Doing What in Reviewing Product Properties?

- (a) Registration Division (RD): Reviews registration of pesticide chemicals (conventional).
- (b) Antimicrobials Division (AD): Reviews registration of antimicrobial pesticide chemicals (conventional).
- (c) Health Effects Division (HED): Reviews product properties of old chemical pesticides (conventional) undergoing reregistration.
- (d) Special Review and Reregistration Division (SRRD): Reviews reregistration of pesticide chemicals (conventional) registered prior to 01/NOV/1984 and pesticides older than 15 years, after expiration of the exclusive use period.
- (e) Biopesticides and Pollution Prevention Division (BPPD): Registration of biopesticides.

## 4. Why is Product Properties Needed?

The regulatory data requirements for product properties are outlined in the Federal Insecticide, Fungicide, and Rodenticide ACT (FIFRA) and the Federal Food, Drug, and Cosmetic Act (FFDCA) As Amended by the Food Quality Protection Act (FQPA) [10]; and the Code of Federal Regulations (CFR), Titles 21 and Title 40§158.150 to §158.190 for chemical pesticides, §158.690 for biochemical pesticides, and §158.740 for microbial pesticides [1,2,3]. Detailed guidance on how to conduct these studies are outlined in OPPTS Test Guidelines Series 830, Product Properties [6]; OPPTS Test Guidelines, Series 880, Biochemical Test Guidelines [7]; OPPTS Test Guidelines, Series 885, Microbial Pesticides Test Guidelines, Overview of Microbial Pest Control Agents [8]; and OPPTS Test Guidelines, Series 810, Product Efficacy

[5]. Listed below are some of the regulatory requirements surrounding the need for product properties:

(a) Identification and characterization of each ingredient in pesticide products; (b) Risk assessment; (c) Environmental Fate assessment; (d) Reentry determination and labeling precautions pertaining to worker protection; (e) Labeling directions pertaining to tank mixes and spray applications; (f) Labeling ingredient statement, precautionary statements, the physical or chemical hazards statement, and the storage and disposal statement; (g) Expressing a product's composition and some properties in the CSFs; (h) Developing the Reregistration Eligibility Decisions (REDs); (i) Public inquiry including, but not limited to: chemical spills, injuries to the flora and fauna, uses, contamination to various compartments of the environment, still birth, drift, degradation, efficacy, fish kills, leaching, runoff, marketing, storage, disposal, transportation, analytical methods, flammability, corrosivity, and explosability.

**5. Product Properties Data Requirements for Registration and Reregistration of Pesticide Chemicals (Conventional):** Refer to the SOP or page 18 of OPPTS Test Guidelines, Series 830, Product properties [6].

**6. Highlighting the Differences Between the Products:** Refer to the SOP.

**7. Confidential Business Information (CBI) and Non-CBI Product Properties**

- (a) Properties Considered CBI: In Group "A" of OPPTS Test Guidelines, Series 830 [6], listed by Guideline Reference Number (GRN) and title - 830.1550 product composition, 830.1600 description of materials used to produce the product, 830.1620 description of production process, 830.1650 description of formulation process, 830.1670 discussion of formation of impurities, 830.1700 preliminary analysis, 830.1750 certified limits, and 830.1800 enforcement analytical method for impurities and ingredients of toxicological concern; all CSFs; nitrosamine and dioxin analysis data, even if none are detected, i.e., below the LOQs.
- (b) Properties Considered Non-CBI: In Group "A"- 830.1550 product identity, 830.1800 enforcement analytical method for the pure active ingredients and related compounds/isomers that are pesticidally active (label claim nominal concentrations), and 830.1900 submittal of samples; all of the physical/chemical properties in Group "B"-830.6302 to 830.7950; and all labels.

**8. Product Properties Studies Requiring Compliance or Noncompliance with the Good Laboratory Practices (GLP) Standards of 40CFR§160**

- (a) Studies that must be conducted in full compliance with the GLP standards of 40CFR§160.135(a) [1,6] - 830.1700 preliminary analysis; 830.6313 stability to normal and elevated temperatures, metals, and metal ions; 830.6317 storage stability; 830.7550 partition coefficient (n-octanol/water, shake flask method), 830.7560 partition coefficient (n-octanol/water, generator column method), 830.7570 partition coefficient (n-octanol/water, estimation by liquid chromatography); 830.7840 water solubility (column elution method or shake flask method), 830.7860 water solubility (generator column method); 830.xxxx solubility in organic solvents; and 830.7950 vapor pressure (no test procedure for 830.xxxx was included in the guidelines [6]).
- (b) The GLP requirements are not applicable to descriptive requirements comprising group

“A” except for GRN 830.1700 preliminary analysis (erroneously cited in the guidelines [6] as requiring GLP standards).

- (c) Studies requiring partial compliance with GLP of 40CFR§160.135(b) [1,6] - The remaining requirements.

## 9. The Self-Certification Program

Stipulated in PR Notice 98-1 on self-certification of product properties data for non-integrated MP & EP formulated using registered technical sources with no intended chemical reaction. The Notice defined “non-integrated production system” and directed registrants/applicants seeking registration or reregistration of pesticides to submit an abstract summary of thirteen physical/chemical properties using a one page Form, 8570-36. A signed and dated self-certification statement, Form 8570-37, must accompany an application. The objectives were to simplify, accelerate the registration and reregistration of all pesticides, achieve consistency, and save paperwork.

## 10. Review of Pesticide Labels and CSFs

- (a) label and CSF of a formulated end-use product (EP)

" \ 2Label ingredient statement: Active ingredient.....24%  
Other Ingredients.....76%  
Total.....100%

**Table I. Columns 13 and 14 of the CSF of an End-Use Product**

Column 13		Column 14	
(a) Amount in lbs	(b) % w/w	(a) % Upper Limit	(b) % Lower Limit
250 Active	25 (24)	(24.72)	(23.28)
350 Inert	35	36.05	33.95
400 Inert	40	41.2	38.8
1000 (total w/w)	100		

Explanations: The source technical is 96% pure. The general formula for calculating the nominal concentration is:  $N = [(w/w \times P) \div 100]$ , where N = nominal concentration, w/w = percentage by weight, and P = chemical purity of the TGAI. Please note the difference between nominal concentration and percentage by weight. Further, the amount for inerts are expressed in percentages by weight, not nominals erroneously required by the regulations, since nominals are based on pure substances, whereas inerts each is composed of a mixture of various components with multiple nominals.

(b) label and CSF of a Technical Grade of Active Ingredient (TGAI)

Label ingredient statement: Active ingredient.....96%  
 Other Ingredients..... 4%  
 Total.....100%

**Table II. Columns 13 and 14 of the CSF of a Manufactured TGAI**

Column 13		Column 14	
(a) Amount, lbs	(b) % w/w (nominal)	(a) % Upper Limit	(b) % Lower Limit
960 (active)	96.0	99	93
15 (impurity)	1.5	2.0	
20 (impurity)	2.0	2.5	
995	99.5		

Explanations: Based on sample analysis using the enforcement analytical method, the pure active ingredient (PAI which is the nominal concentration) of the TGAI is 96% and the nominal concentration of two impurities are 1.5% and 2.0% for a total method accountability = 99.5%, equivalent to 995 pounds. Because batch production or the actual yield was 1000 pounds, 5 pounds or 0.5% of the amount was not accounted for by the method, noting that method accountability for manufactured products  $\geq 98\%$  is acceptable [3]. If the amount is calculated back from the determined percentage nominal, a second nominal concentration for the TGAI can be calculated at 96.5% based on the percentage recovery relative to the amount recovered ( $960 \div 995$ ). A third nominal for the TGAI can be calculated at 95.0% ( $960 \div 1010$ ) if considerations were given to the expected production yield, meaning the yield of 1000 pounds should have been 1010 based on the molar ratios of the reactants, their purities, manufacturing process/conditions and purification techniques, noting that production yield can vary considerably, reported at 17% in one technical. Considerable variations can also be attributed to differences between batches within the same production site, as well as between production sites.

From the above notes, it is apparent that the amount column in the CSF adds to confusion when entering TGAI in a revised CSF (the present CSF is geared toward formulated end-use products). For formulated products, the amount reported in the CSF can range from as little as 16 ounces (alkaloids) to a batch of 100, 1000 or a million pounds from which the CSF reviewer

checks to see if the percentages w/w are correct. This arithmetic is irrelevant to the review of a CSF. Further, any error by the applicant in converting from amounts to percentage by weight will be captured in the material balance of 100%. The actual amounts are reported to other science disciplines for risk/benefit assessments.

## **II. REVIEW FORMS AND SAMPLE REVIEWS:** Please refer to the SOP.

## **III. EXPLANATIONS OF CERTAIN REGULATORY CAVEATS**

### **1. Proposed Upgrades to the Table of Requirements In OPPTS Test Guidelines, Series 830 [6]**

The Proposed Revisions would make it easier for the regulated pesticide industry to follow the regulations and comply with the specific requirements. The proposed revisions are intended to address many issues the answer of which can not be found in the regulations. Examples: what are the requirements for a product manufactured or formulated from non-registered sources or sources of an unknown composition to the EPA? Similarly, what are the requirements for a pure active ingredient (PAI) and MP/EP technicals? The agency regards the definition for non-integrated formulation system stipulated in PR Notice 98-1 [9] as a step in the right direction toward classifying all products into two major classes: "non-integrated" accounting for approximately two thirds of all pesticides, and "integrated" accounting for the other one-third. This classification focuses the Agency's attention to re-structuring the table of requirements and propose a definition, classification, and requirements for integrated products (Table III).

The proposed revisions to the table of requirements are as follows: (a) Delete the column citing the outdated Pesticide Assessment Guideline (1982) numbers; (b) Combine three methods for partition coefficient in one requirement (GRNs 8570.7550, 830.7560 & 830.7570); (c) Combine two methods for water solubility in one requirement (GRNs 830.7840 & 830.7850); (d) Include a test for solubility in organic solvents (GRN-xxxx); (e) GRNs 830.7050 (UV/VIS absorption) and 830.7520 (Particle size, fiber length, and diameter distribution) should be moved to Environmental Fate Guidelines, Series 835 since the former pertains to photodegradation and the latter pertains to drift to non-target organisms, both are Environmental Fate requirements; (f) GRN 830.7520 was inadvertently omitted from the table of requirements; (g) Designate the last two columns for non-integrated products and the case-by case for submittal of samples (GRN 830.1900) can be explained as such: "in situations of interference and/or chemical reaction resulting in the formation of new ingredients" to include: preliminary analysis (GRNs 830.1700), and modified or new enforcement analytical methods (GRN 830.1800); (h) Delete the requirement for GRN 830.1650 (formulation process) for manufactured products; (i) Delete the requirement for GRN 830.1620 (production process) for formulated products; and (j) Delete the requirement for GRN 830.1670 (discussion of formation of impurities) for non-integrated products.

### **2. Proposed Upgrades to OPPTS Test Guidelines, Series 830 [6]**

(a) Integrate the self-certification program stipulated in PR Notice 98-1 [9]; (b) Add a definition for non-integrated products, first defined in PRN 98-1 [9]; (c) A definition for pure active

ingredient (PAI): equals to or more than 99% pure [this definition can not be found in the regulations].?; (d) Add a definition for insolubility in water: less than  $\leq 1.00$  ppm; (e) Allow ranges for the pH (within 2 units, e.g. 7-9) and density (not to exceed 25% of the lower value, e.g. 40 to 50 lb/ft<sup>3</sup>); (f) Add a definition and guidance on repacks: “no data except when diluted”; (g) Add a correct definition for to the nominal concentration, cited in this manuscript;

**Table III. Proposed Classification and Product Properties Data Requirements for Registration or Reregistration of Integrated Pesticide Products**

<i>Number and Type of Each Class</i>		<i>Data Requirements</i>
1	TGAI	Listed in the table of requirements
2	PAI	Same as for the TGAI using the PAI as the test substance
3 & 4	MP/EP that are TGAIs	All the requirements where applicable <sup>1</sup>
5 & 6	MP/EP manufactured from registered sources	All the requirements where applicable <sup>1</sup>
7 & 8	MP/EP manufactured from non-registered sources	All the requirements where applicable <sup>1</sup> . Carryover impurities must be identified on all the CSFs of the data owner
9 & 10	MP/EP manufactured from sources of an unknown composition to the EPA [that does not permit its inspection by the Agency under FIFRA sec.9(a) prior to its use in the process]	All the requirements where applicable on each MP/EP and on each source <sup>1</sup> in the product prior to manufacturing or by isolating each source. If the sources can not be isolated, data are required on the practical equivalent to the TGAI of each source. Carryover impurities must be identified on all CSFs of the data owner
11 & 12	MP/EP formulated from non-registered sources	Same as for non-integrated products only if the full data on each source was submitted to the Agency and found adequate. Carryover impurities must be identified on all the CSFs of the data owner
13 & 14	MP/EP formulated from sources of an unknown composition to the EPA	Same as for non-integrated products plus the full data requirements on each source in the product prior to formulation or by isolating each source. If the sources can not be isolated, data are required on the practical equivalent to the TGAI of each source. If known, carryover impurities must be identified on all the CSFs of the data owner
15 & 16	MP/EP formulated from registered sources in which a chemical reaction took place resulting in the formation of new ingredients	All the requirements where applicable <sup>1</sup>

<sup>1</sup>GRNs 830.1550 to 830.7950 using the test substances recommended in the table of requirements, also refer to the conditional requirements listed as footnotes to the table in 40 CFR §158.190 [1].

(h) Specificity in the following terms: integrated vs. non-integrated products, manufactured vs. formulated products, TGAI vs. PAI, and nominal concentration vs. percentage by weight;

(i) Chemical formula change: a change in manufacturing and/or site, data requirements, and a change in formulation and/or site, data requirements; (j) Method accountability for manufactured products  $\geq 98\%$ ; (k) Concentrations for inert ingredients to be expressed as percentage by weight (no nominals because each is composed of multiple ingredients) with multiple nominals; (l) Wider limits for the ingredients can be accepted if explained as per the regulations of 40 CFR §158.175(c); (m) For consistency with the regulations in 40 CFR §158.150, delete the requirements for lower limits for impurities; (n) Specific guidance to the GLP requirements; (o) Aged and number of samples needed for analysis of: halogenated dibenzodioxins, dibenzofurans, hexa & penta chlorobenzene, anilines, hydrazines, sodium nitrite, list 1 inerts, and others of toxicological concern similar to the recommendations for nitrosamines in page 9 of the guidelines; (p) Low level of quantitation (LOQ) similar to those in 40 CFR §766.27 and level of acceptability for ingredients of toxicological concern and what should be listed on pesticide labels?; (r) Upgrade GRN 830.1700 (preliminary analysis) to explain what is required for non-integrated products; and (s) Re-define integrated products to mean “all products except non-integrated.”

#### IV. REFERENCES

1. *Code of Federal Regulations, Title 40, Parts §158.150 to §158-190, §158.690, §158.640 & §160.*
2. *Code of Federal Regulations, Title 21.*
3. *Code of Federal Regulations, Title 40 §766.27.*
4. *Federal Register Notice: 49(207)FR42863, 24/OCT/1984.*
5. *OPPTS Test Guidelines, Series 810, Product Efficacy.*
6. *OPPTS Test Guidelines, Series 830, Product Properties, EPA 712-C-96, August, 1996.*
7. *OPPTS Test Guidelines, Series 880, Biochemical Test Guidelines.*
8. *OPPTS Test Guidelines, Series 885, Microbial Pesticides Test Guidelines, Overview of Microbial Pest Control Agents.*
9. *Pesticide Regulations 98-1, entitled "Self-Certification of Product Chemistry Data."*
10. *The Federal Insecticide, Fungicide, and Rodenticide ACT (FIFRA) and the Federal Food, Drug, and Cosmetic Act (FFDCA) As Amended by the Food Quality Protection Act (FQPA) of August 3, 1996.*
11. *Malak, Sami, and Deborah McCall (2002), Proposed Revisions to Product Chemistry Data Requirements for Registration of Pesticide Chemicals, ACS Symposium Series 824, Chapter 23 (15 pages), Capturing and Reporting Electronic Data, edited by Willa Garner, Rodney M. Bennett, and Markus Jensen.*

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## **Introducing QA/G-11: EPA's New Guidance on QA for Environmental Technology**

Gary L. Johnson, U.S. EPA; Kevin J. Hull, Neptune and Company; Joseph D. Evans, SAIC

*EPA has developed a new guidance document on quality assurance and quality control practices for the design, fabrication/construction, testing, and operation of technology applied to environmental programs. This paper discusses where and how such practices may be applied during the planning, implementation, and evaluation phases of a project.*

### **INTRODUCTION**

For over 20 years, the U.S. Environmental Protection Agency (EPA) has published requirements and guidance documents on applying quality assurance (QA) and quality control (QC) practices to environmental programs. The basis of QA and QC practices was the American National Standard ANSI/ASQC E4:1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs*. The environmental programs encompassed a variety of activities, including planning for data collection, field sampling, and laboratory analysis, and pertain to all environmental media.

Recently, EPA completed work on a new document that provides guidance on developing and applying QA and QC practices to environmental technology. Such technology includes pollution control devices and systems, waste treatment processes and storage facilities, and site remediation technologies and their components that may be utilized to remove pollutants or contaminants from or prevent them from entering the environment. Examples include wet scrubbers (air), soil washing (soil), granulated activated carbon unit (water), and filtration (air, water). Moreover, this term also applies to methods or techniques used for pollution prevention, waste reduction, or containment of contamination to prevent further movement of the contaminants, such as capping, solidification or vitrification, and biological treatment. While many of the underlying quality principles are the same for data collection and environmental technology, the QA and QC practices needed to ensure that quality objectives and criteria are satisfied are different. Traditionally, environmental data collection and analysis work is founded in the physical, chemical, and biological sciences primarily. The use of technology systems for pollution control, waste treatment, and waste reduction is based chiefly on the engineering sciences. These differences are reflected in how QA and QC are defined and applied.

Based on the specifications found in the E4 standard, the EPA has developed the QA/G-11 guidance document to describe QA and QC practices for use in supporting the design, construction, and operation of environmental technology. Entitled *Guidance on Quality Assurance for Environmental Technology Design, Construction, and Operation*, the G-11 document is written for project managers and quality practitioners who need to apply QA and QC to engineering technology in environmental programs, and includes discussions of general

principles, planning and management, design of systems, fabrication of system components and construction, operation and maintenance of systems, and assessment and verification methods.

## SCOPE OF THE GUIDANCE

This paper will describe the G-11 guidance document and its intended use. In doing so, it is equally important to discuss what the guidance does not do as it is to show what it does. First of all, G-11 is a *guidance document*. This means that it does not impose requirements. EPA requirements are imposed through regulations, such as the Federal Acquisition Regulations (FAR), or through contractual and assistance agreements. The G-11 text provides a guide on how QA and QC may be applied to projects involving environmental technology. Where processes are discussed or suggested, G-11 may not be the only way to achieve the same result. It is a non-mandatory guide.

Second, engineering projects come in different sizes and not all involve environmental technology. G-11 is intended to address a “sub-set” of those engineering projects that apply technology to environmental projects to water treatment, pollution control, waste clean-up and remediation, source reduction, etc. G-11 is not intended to be a guide to engineering project management for exceptionally large projects even though many of the underlying principles in G-11 could be applied to them. Rather, G-11 is intended to apply to the size and type of technology usually addressed by EPA and its State, municipal, and private partners in environmental programs.

The G-11 guidance document is organized in a “plan-do-check-act” logic flow typical of engineering projects. Within this framework, G-11 will document where and how appropriate QA and QC practices may be implemented during the course of the design, fabrication and construction, testing, and operation of the technology being applied to environmental problems.

## APPLICABLE QUALITY PRINCIPLES

The following general guiding principles (which are adapted from the E4 standard) underlay the structure and content of this guidance document:

**Quality planning** – All work involving the design, construction, and operation of environmental technology should be planned, documented, and controlled as needed to achieve conformance with approved quality criteria.

**Design of systems** – Processes and procedures should be established and implemented to ensure that environmental technologies are designed using sound engineering/scientific principles and appropriate quality standards.

**Construction of systems and components** – Construction, fabrication, manufacture, and erection of systems and components should be performed under appropriately controlled conditions according to the drawings and specifications of the approved design.

**Operation of systems** – Environmental technologies should be operated in accordance

with approved design documentation and operating instructions and guides.

**Assessment and response** – Work performed during the design, construction, and operation of environmental technology that affects quality should be assessed regularly to ensure that approved planning and design specifications and operating guides are being implemented as prescribed.

**Verification and acceptance** – The performance of environmental technology should be verified according to its intended use as documented in approved design specifications. When acceptance criteria are not met, deficiencies should be resolved and reassessments conducted as necessary.

Note that these principles span the three main phases of EPA's Quality System: planning (principles 1–2), implementation (principles 3–4), and assessment (principles 5–6).

The guidance document elaborates on each of these six general guiding principles by presenting a discussion of the lower-tier basic quality principles that are applicable to them. These lower-tier quality principles are as follows:

#### Quality Planning

- Adherence to quality principles and practices in project management, not only in the planning stages but throughout the project, is key for the successful implementation of an environmental technology.
- Every organization implementing an environmental technology should be driven by a policy that defines quality expectations.
- Organizational structure should be defined at every level in which QA and QC activities are necessary.
- Different phases of a project call for staffing of appropriate and competent personnel for the following activities and organizations: site owner/management, design, construction, and operation.
- Effective project planning and implementation depend upon good coordination among all parties, which, in turn, depends on effective communication among those same parties.
- Documents should be controlled to ensure that the correct documents are being used.

#### Design of Systems

- The engineering/design professional, contractor, or subcontractor (the design team) should establish and maintain documented procedures to control and verify the design of the environmental technology in order to ensure that QA specifications are met.
- Organizational and technical interfaces should be identified during planning stages and controlled appropriately during the design efforts.
- Prior to the start of the design phase, the owner and the design, construction, and operations teams, separately as well as collectively, should identify all pertinent design characteristics for the project.
- The responsible design organization(s) should define, manage, and document the design activities on a timely basis and to the level of detail appropriate to permit the design process to be carried out correctly, effectively, and in a timely manner and to permit verification that the design meets specifications.
- Design output should be documented and expressed in terms that can be verified against design criteria (including specific acceptance criteria) and validated.
- Operation and maintenance (O&M) specifications should be considered in each phase of project planning, design, construction, and start-up.
- At appropriate stages of design (e.g., 30, 60, and 90%), formal documented reviews of the design are planned and conducted.

- The design professional should establish and maintain documented procedures for identification, collection, indexing, access, filing, storage, maintenance, and disposition of design output documents including drawings, calculations, and results, as well as references, standards, codes, design basis, and assumptions used in the design process.
- The verification process evaluates the completeness, correctness, and conformance or compliance of the design in terms of meeting contractual, method, or procedural specifications.
- Design validation is performed through assessments to ensure that the designed products, processes, and procedures conform to defined user needs.
- All design changes and modifications must be identified, documented, reviewed, and approved by authorized personnel before their implementation using clearly defined documented procedures. (Even though G-11 is a guidance document, some activities must be performed as required by contracts, statutes, and codes and regulations.)

### Construction of Systems and Components

- Quality in the construction, fabrication, and installation phase of a project is achieved by establishing, implementing, and maintaining documented procedures to control and verify that technical specifications and QA and QC criteria are met.
- Project site specifications should be established and documented.
- Management should identify resources available, how they are allocated, and associated responsibilities for resource allocation.
- The responsible party or technology developer should establish contracting requirements for project construction.
- The responsible party and participating organizations, including the design professional, construction contractor, and facility operators, should ensure that procured products and services meet established technical and QA objectives and that they perform as specified.
- Early construction planning by the responsible party, design professional, and constructor enables schedule milestones to be included in the construction contract.
- During the construction and fabrication of system components, the constructor's (and all subcontractors') estimates should be tracked, refined, and updated.
- The constructor should establish a documented plan to control and track purchasing, receiving, special storage, and in-storage maintenance of materials for the project and the time frame.
- An important part of the work planning process is to identify the items and processes to be inspected or tested, the parameters or characteristics to be evaluated, the techniques to be used, the acceptance criteria, any hold points, and the organization responsible for performing the tests and inspections.
- During the planning phase of the project, specifications for construction completion certification and approvals of external agencies and other groups should be established, documented, and communicated with appropriate individuals.

### Operation of Systems

- O&M factors influence life-cycle costs, continuity of service, durability, public health and safety, environmental impact, and other features of the completed environmental technology project/program/facility.
- The developer may select from a number of options providing for consideration of the various O&M issues as they influence design, construction, and operation of the environmental technology.
- Decisions made during the design phase relating to site selection and access, process choice, equipment selection, and other elements of the project will impact O&M of the completed project and limit flexibility in subsequent phases of the project.
- The construction phase of the project provides an opportunity for the developer's O&M coordinator to make the transition from the advisory and review activities of the design phase to more active roles during the construction phase.
- The O&M staff are key players in the start-up of any project.
- Documented procedures should be established prior to the start of the operating phase and refined, fine-tuned, and updated, as needed, for all substantial activities that constitute the system operation.

- The O&M organization should establish and maintain documented procedures for receiving, in-process, and final inspection and testing in order to verify that specifications are achieved. Provided in this section are inspection and testing specifications for engineering applications.
- Documented procedures should be established and maintained for handling, storage, packaging, preservation, and delivery of product.

#### Assessment and Response

- Assessment provides the basic program structure to ensure that quality specifications are maintained.

#### Verification and Acceptance

- Verification is confirmation by examination and provision of objective evidence that specified requirements have been fulfilled. Though it is related to the concept of assessment, verification is usually considered an ongoing line management responsibility, rather than as independent oversight.

## INTENDED AUDIENCE

This document is intended to provide clear, coherent, and user-friendly guidance that will serve as a standard tool for managers and officials in the EPA and other State and Federal agencies for implementing quality systems when deploying environmental technologies. The intended audience for this guidance includes QA officers, site remedial project managers, persons responsible for site clean-ups, and other environmental professionals involved with environmental technology design, construction, and operation. It is designed to assist all those responsible for writing, reviewing, or approving Quality Management Plans or Quality Assurance Project Plans for environmental technology projects.

## REFERENCES

2. U.S. EPA, *Guidance on Quality Assurance for Environmental Technology Design, Construction, and Operation* (EPA/QA G-11), Quality Staff, Washington, DC (Peer Review Draft).
2. ANSI/ASQC E4:1994, *Specifications and Guidelines for Quality Systems for Environmental Data Collection and Environmental Technology Programs*, American National Standard, American Society for Quality, Milwaukee, WI (January 1995).

## Environmental Sampling for Conventional UXO Sites

Mrs. Deborah Dixon Walker, RHSP, CHMM,  
US Army Corp of Engineers, Engineering & Support Center – Huntsville

*Many UXO are to be found on Department of Defense (DoD) and Formerly Used Defense Sites (FUDS) property located in environmentally sensitive areas. Recently, regulatory and stakeholder concerns about environmental contamination related to UXO have increased. Limited environmental sampling has been incorporated as an optional task in the standard OE Engineering Evaluation and Cost Analysis (EE/CA) Scope of Work (SOW) for all future projects.*

Many Unexploded Ordnance (UXO) are to be found on Department of Defense (DoD) and Formerly Used Defense Sites (FUDS) property located in environmentally sensitive areas. Recently, regulatory and stakeholder concerns about environmental contamination related to UXO have increased. The FUDS funding process provides for separate funding program categories for Hazardous, Toxic, and Radioactive Waste (HTRW) projects and Ordnance and Explosives (OE) projects, even if those projects are for the same location. A common goal for each program category, however, is to achieve site closeout in a safe, environmentally responsible, and cost-effective manner. It is critical to coordinate efforts to obtain this goal of site closeout because sites are commonly addressed sequentially, beginning with OE before focusing on HTRW. Rarely are both implemented at the same time due to differing safety priorities or budgets. To minimize risk to HTRW workers, the physical hazard of OE must be minimized or removed before significant HTRW work is performed. Any explosive contaminants in environmental media that remain are the responsibility of the HTRW program.

Recent USACE guidance (EM 1110-1-1200) addresses the development of an integrated Conceptual Site Model (CSM) for OE and HTRW projects. The CSM is an iterative tool used during the USACE Technical Project Planning (TPP) Process. The TPP process is a systematic planning process analogous to the US Environmental Protection Agency (USEPA) Data Quality Objective (DQO) process. During the TPP process, several OE projects conducted by CEHNC have incorporated limited environmental sampling at the request of regulatory participants (see Table 1). The environmental sampling data is incorporated in the integrated CSM. OE projects that collect environmental sampling data do so with the intent that, due to the separation of funding programs, if environmental contamination were found to be a problem, it would be cleaned up under either a new or an existing HTRW project. Limited sampling and analysis can be executed during the OE Engineering Evaluation and Cost Analysis (EE/CA) field effort if funds are available. Therefore, limited environmental sampling has been incorporated as an optional task in the standard OE EE/CA Scope of Work (SOW) for all future projects. Future projects that include sampling based on the standard SOW requirement are listed in Table 2.

Table 1 - Recent Conventional UXO Projects with Environmental Sampling

Bergstrom AFB, TX  
Camp Edwards, MA\*\*  
Camp Ibis, CA\*  
Camp Swift, TX  
Culebra Island Wildlife Refuge, PR  
Savanna Army Depot, IL\*  
5 Points OLF, TX

\*Sampling Planned

\*\* Additional Sampling Planned

Table 2 – Projects with New Standard Language

Frankford Arsenal, PA  
Williams Field Bomb Target Range, AZ  
Kirtland AFB, NM  
Camp Wheeler, GA  
Spencer Range, TN  
Fort Miles, DE

The EE/CA SOW provides a starting point for project planning. It is based on a biased sampling approach intended to determine if contamination exists at locations that would represent “worst-case” contamination. It includes collection of ten (10) samples to be analyzed for secondary explosives and their breakdown products and RCRA Metals (see Table 3).

Table 3 - Analytes of Interest

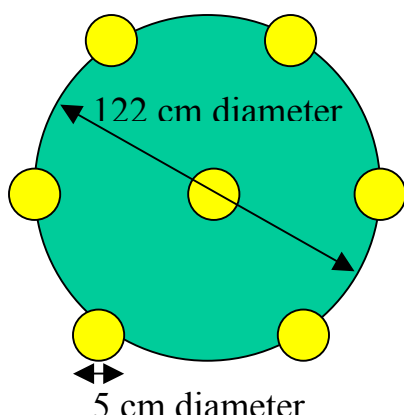
RCRA Metals:	Explosives and Explosive Breakdown Products:
Arsenic	2-Nitrotoluene (2-NT)
Barium	3-Nitrotoluene (3-NT)
Cadmium	4-Nitrotoluene (4-NT)
Chromium	2,4-Dinitrotoluene (2,4-DNT)
Lead	2,6-Dinitrotoluene (2,6-DNT)
Mercury	2,4,6-Trinitrotoluene (TNT)
Selenium	4-Amino-2,6-dinitrotoluene (4-Am-2,6-DNT)
Silver	2-Amino-4,6-dinitrotoluene (2-Am-4,6-DNT)
	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)
	Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
	Methyl-2,4,6-trinitrophenylnitramine (Tetryl)
	Nitrobenzene (NB)
	1,3-Dinitrobenzene (1,3-DNB)
	1,3,5-Trinitrobenzene (TNB)

Soil sampling locations identified for consideration include:

- Samples before and after on-site detonation of OE for each type of OE (also referred to as pre- and post blow-in-place (BIP) sampling)
- Samples at known target impact areas, heavily OE contaminated areas, or firing points
- Background samples

Target impact areas are considered worst case due to the volume of OE directed at that area. Firing points are of concern due to the potential for residual propellant contamination. Pre-detonation samples are required to be discrete samples located as near to the item to be detonated as is safe and feasible. Post-detonation and target samples are required to be composite samples based on the Cold Regions Research And Engineering Laboratory (CRREL) 7-sample wheel approach (see Figure 1) (as described in ERDC SR96-15: [http://www.crrel.usace.army.mil/techpub/CRREL\\_Reports/reports/SR96\\_15.pdf](http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR96_15.pdf)). Surface water samples are to be considered if a flowing water source is located on site that leaves the site. The SOW emphasizes that sampling requirements (numbers or analyses) may be modified during the TPP.

Figure 1 – CRREL 7-Point Wheel Sampling Approach



During the TPP, it is important to develop data quality objectives (DQOs), preferably identifying any chemical-specific Applicable or Relevant and Appropriate Requirements (ARARs) or requirements that are to be considered (TBCs) and future land use. Some potential ARARs/TBCs for explosive contaminants in soil are provided in Table 4.

Table 4 – Potential ARARs/TBCs for Explosive Contaminants in Soil <sup>(1)</sup>														
	2-NT	3-NT	4-NT	2,4-DNT	2,6-DNT	TNT	4-Am-2,6-DNT	2-Am-4,6-DNT	HMX	RDX	Tetryl	NB	1,3-DNB	TNB
Industrial Land Use														
Region III RBC <sup>(2)</sup>	20000	41000	20000	8.4 <sup>(3)</sup>	8.4 <sup>(3)</sup>	190	120	120	100000	52	20000		200	61000
Region VI SL <sup>(2,4)</sup>	11000	11000	11000	2.8 <sup>(3)</sup>	2.8 <sup>(3)</sup>	64	NE	NE	34000	17	6800	110	68	21000
Region IX PRG <sup>(2)</sup>	1000	1000	1000	2.5 <sup>(3)</sup>	2.5 <sup>(3)</sup>	57	NE	NE	31000	16	6200	100	62	18000
Arizona SRL	NE	6800	6800	28 <sup>(3)</sup>	28 <sup>(3)</sup>	340	NE	NE	34000	170	6800	94	68	34
Pennsylvania MSC (Direct Contact, 0-2')	NE	NE	NE	260	2800	1400	NE	NE	NE	NE	NE	1400	280	NE
Residential Land Use														
Region III RBC <sup>(2)</sup>	780	1600	780	0.94 <sup>(4)</sup>	0.94 <sup>(4)</sup>	21	4.7	4.7	3900	5.8	780		7.8	2300
Region VI SL <sup>(2)</sup>	780	780	780	0.72 <sup>(4)</sup>	0.72 <sup>(4)</sup>	16	NE	NE	3100	4.4	610	20	6.1	1800
Region IX PRG <sup>(2)</sup>	370	370	370	0.72 <sup>(4)</sup>	0.72 <sup>(4)</sup>	16	NE	NE	3100	4.4	610	20	6.1	1800
Arizona SRL	NE	650	650	6.5 <sup>(4)</sup>	6.5 <sup>(4)</sup>	33	NE	NE	3300	40	650	18	6.5	3.3
Pennsylvania MSC (Direct Contact, 0-15')	NE	NE	NE	58	220	110	NE	NE	NE	NE	NE	110	22	NE

<sup>(1)</sup> – All concentrations are in milligrams per kilogram (mg/kg).

<sup>(2)</sup> – Concentrations are reported in scientific notation to 2 significant figures in source table and have been rounded to 2 significant figures for this table.

<sup>(3)</sup> – Value for dinitrotoluene mixture. Value for specific isomer is higher.

<sup>(4)</sup> – Concentrations for the Industrial-Outdoor Worker.

MSC – Medium Specific Concentration

SL – Screening Level

PRG – Preliminary Remediation Goal

SRL – Soil Remediation Level

RBC – Risk Based Concentration

NE – Not Established

Sources:

Arizona: [http://www.sosaz.com/public\\_services/Title\\_18/18-07.htm](http://www.sosaz.com/public_services/Title_18/18-07.htm)

Pennsylvania: [http://www.dep.state.pa.us/dep/deputate/airwaste/wm/landrecy/MSCs/Table\\_3A.xls](http://www.dep.state.pa.us/dep/deputate/airwaste/wm/landrecy/MSCs/Table_3A.xls), November 24, 2001

Region III RBC: <http://www.epa.gov/reg3hwmd/risk/rbc1002.XLS>, October 2002

Region VI Human Health Medium-Specific Screening Levels: [http://www.epa.gov/Arkansas/6pd/rcra\\_c/pd-n/02screenexpanded.xls](http://www.epa.gov/Arkansas/6pd/rcra_c/pd-n/02screenexpanded.xls), November 2002, as modified February 18, 2003

Region IX PRG: <http://www.epa.gov/region09/waste/sfund/prg/files/02prgstable.xls>, October 2002, as modified February 10, 2003

Project planning for environmental sampling is addressed as part of the TPP and documented in project-specific Sampling and Analysis Plans. USACE HTRW quality control (QC) and quality assurance (QA) requirements are followed for sampling and analysis on OE projects. Specific USACE guidance that applies is listed in Table 5 and available for download at <http://www.usace.army.mil/publications/>.

Table 5 – Applicable USACE Guidance		
EM 200-1-2	Technical Project Planning (TPP) Process	31 Aug 1998
EM 200-1-3	Requirements for the Preparation of Sampling and Analysis Plans	01 February 2001
EM 200-1-6	Chemical Quality Assurance for HTRW Projects	10 Oct 1997
EM 1110-1-1200	Conceptual Site Models for Ordnance and Explosives (OE) and Hazardous, Toxic, and Radioactive Waste (HTRW) Projects	3 February 2003
ER 1110-1-263	U.S. Army Corps of Engineers Chemical Data Quality Management for Hazardous, Toxic, Radioactive Waste Remedial Activities	30 April 1998
HNC Interim Guidance Document 01-02	Implementation of Technical Project Planning (TPP) for Ordnance and Explosives (OE) Formerly Used Defense Sites (FUDS) Projects	27 June 2001
HNC Data Item Description (DID) OE-005-10.01	Environmental Sampling and Analysis Plan	1 October 2002

Lessons learned to date include:

- OE personnel typically have different skill sets than HTRW personnel, so cross-training is key to getting quality data.
- TPP process needs to include discussion of environmental sampling data use, particularly if numeric goals have not been established.
- More environmental contamination can be expected if low order detonation had occurred

Future activities include collection of sample data based on standard approach. The data set from these projects will be examined to identify any trends for environmental contamination from UXO at DoD sites. All data available currently is based on project-specific approaches determined during TPP, so it is difficult to determine whether trends exist.

## **A Guidance is Developed, the Story Behind QA/G-5S**

John Warren, Quality Staff

*QA/G-5S, Guidance on Choosing a Sampling Design for Environmental Data Collection, was released in December 2002, and is the most complex document issued to date. This guidance was issued in response to demands from the environmental community for help in selecting the appropriate data collection design appropriate to their specific circumstance. A discussion of how this document was developed, where it fits into the overall series of guidance issued by the Quality Staff, how it relates to Visual Sampling Plan, and what future features will be added to the guidance will be the subject of this talk.*

## Visual Sample Plan (VSP) - FIELDS Integration

Brent Pulsipher, John Wilson, Richard Gilbert, Nancy Hassig, Deb Carlson,  
Pacific Northwest National Laboratory  
John Bing-Canar, Brian Cooper, Chuck Roth  
U.S. EPA-Region 5

*Two software packages, VSP 2.0 and Fields 3.0, are being used by environmental scientists to plan the number and type of samples required to meet project objectives, display those samples on maps, query a database of past sample results, produce spatial models of the data, and analyze the data in order to arrive at defensible decisions. VSP 2.0 is an interactive tool to calculate optimal sample size and optimal sample location based on user goals, risk tolerance, and variability in the environment and in lab methods. Fields is a set of tools to explore the sample results in a variety of ways to make defensible decisions with quantified levels of risk and uncertainty. Fields 3.0 has a limited sample design module, allowing for only one or two sampling goals, such as compare an average to a fixed standard. VSP 2.0 has over 20 sampling goals, allowing the user to input site-specific assumptions such as non-normality of sample results, separate variability between field and laboratory measurements, make two-sample comparisons, perform confidence interval estimation, use sequential search sampling methods, and much more. Over 1000 copies of VSP are in use today. FIELDS is used in nine of the ten EPA regions, by state regulatory agencies, and most recently by several international countries. Both software packages have been peer-reviewed, enjoy broad usage, and have been accepted by regulatory agencies as well as site project managers as key tools to help collect data and make environmental cleanup decisions.*

*Recently, the two software packages were integrated, allowing the user to take advantage of the many design options of VSP, and the analysis and modeling options of FIELDS. The transition between the two is simple for the user – VSP can be called from within FIELDS, automatically passing a map to VSP and automatically retrieving sample locations and design information when the user returns to FIELDS.*

*This paper will describe the integration, give a demonstration of the integrated package, and give users download instructions and software requirements for running the integrated package.*

### VSP Capabilities

Visual Sample Plan is currently a sampling/survey design and analysis package that supports characterization and assessment of surface soils, subsurface soil layers, sediments, building surfaces, and unexploded ordnance (UXO). The underlying methodology employs statistically defensible approaches and has strong Data Quality Objectives (DQO) Process underpinnings. The objective is to ensure that the right type, quality, and quantity of data are gathered to support confident decisions. It allows real-time evaluation of the tradeoffs between increased confidence in decisions and costs or number of samples required. VSP answers the questions of how many samples are required and where should I obtain samples.

Designed for the non-statistician, VSP is a visual, map-based tool that is organized around the

possible data uses. Before developing a data-gathering plan, each user must determine what they will do with the data to support their decision-making process. VSP currently supports the following sampling goals or objectives.

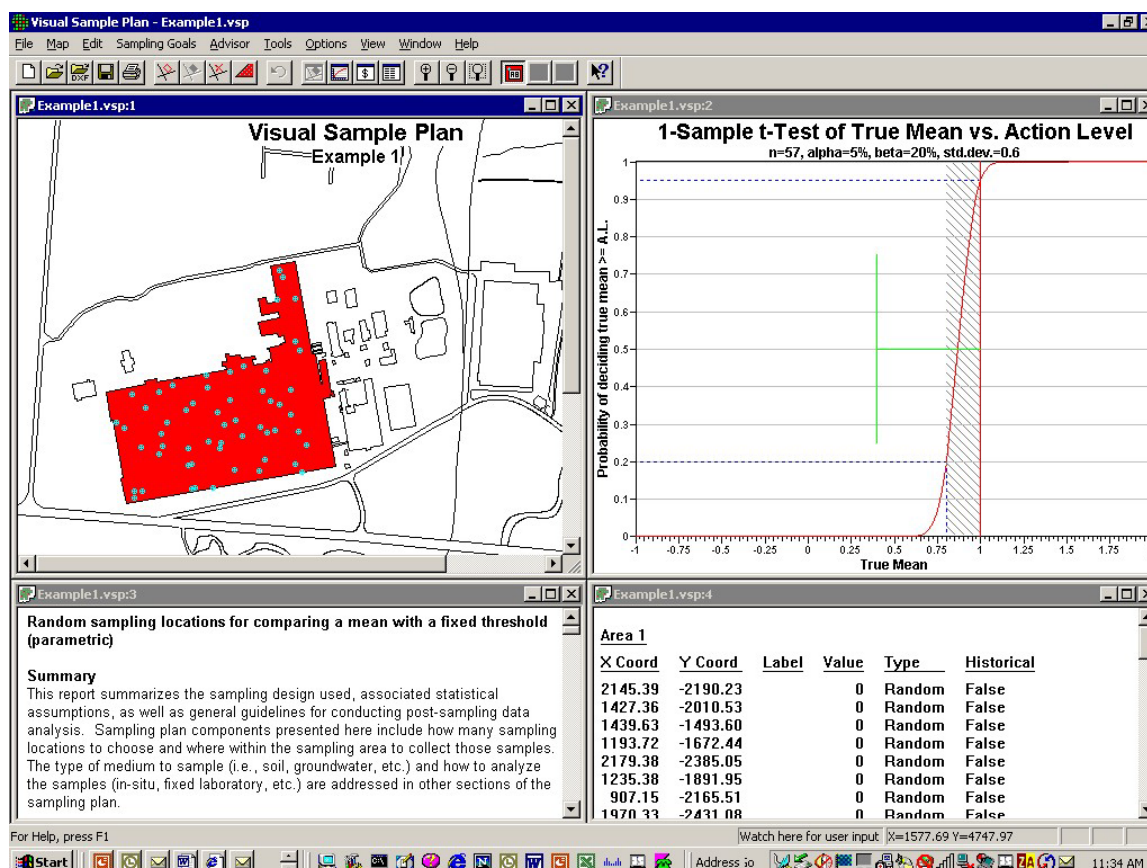
- Compare Average Against a Threshold
- Compare Proportion Against a Threshold
- Compare Average or Proportion Against Reference Data (background)
- Find Hot Spot
- Find UXO Target Area
- Demonstrate Low Probability of UXO Presence
- Develop Confidence Interval
- Estimate a Mean
- Delineate Boundary of Contaminated Zone

Several options exist for the type for sampling design that might be appropriate for each of the above sampling goals. Both statistically-based sampling and non-statistical sampling approaches are available including:

- Simple Random Sampling
- Systematic Grid Sampling
- Non-Normal Distributional Approaches
- Sequential Sampling
- Stratified Sampling
- Rank-Set Sampling
- Adaptive Cluster Sampling
- Continuous Transect Sampling
- Judgmental Sampling

VSP has a number of unique, special features to facilitate use and support defensibility. Some of the diagnostic graphics are interactive, allowing immediate evaluation of tradeoffs between data quality objectives (DQO) requirements and costs. Sample locations are automatically displayed on maps and easily output to files that can be transferred to GPS units in support of in-field sampling and analysis activities. With each sampling plan, a 3-5 page report is automatically generated that documents all the site sample area information, the sample locations, map, diagnostic graphics, statistical assumptions, any formulas used, costs, and sensitivity analyses. The sensitivity analysis table is interactive and can be customized for each user. Finally, online help and technical documentation of the statistical methods are also freely available.

Figure 1 illustrates a typical VSP session. The map view is shown in the upper left quadrant, the graphical diagnostics are shown in the upper right quadrant, the report generator is shown in the lower left quadrant, and the sample coordinates are shown in the lower right quadrant.



**Figure 1**

### FIELDs Capabilities

The FIELDs (Field Environmental Decision Support) Team at the U.S. EPA Region 5 has developed a set of tools that integrate the power of geographic information systems (GIS), imaging software, global positioning system (GPS), and data analysis technology in order to characterize contamination in soils and sediment. The FIELDs Tools (current version is 3.5) are a collection of ArcView extensions that utilize published methodologies for each step in the characterization process. These extensions include Sample Design, Database Query, Geospatial modeling and Analysis, and Human Health and Ecological Risk Assessment along with a link to F/S Plus, the FIELDs stand-alone data analysis and display software jointly developed with SADA at the University of Tennessee Knoxville. The goal of the FIELDs software development team is to provide decision support tools useable to most technical staff at minimum cost. The FIELDs Tools extensions for ArcView are written in Avenue, C++, and Visual Basic. The Sample Design module allows a user to design statistically-based sample designs (random, stratified random, and gridded) and upload these designs to a GPS unit in order to navigate to sample locations. The parameters used to create the sample design (e.g., number of sample locations, sample area, false negative values) are exported as a table that can be included in a report. Once the samples are collected, lab analyzed, the FIELDs Tools' Database Query module can be used to import the data. FIELDs can retrieve data from a table using the FIELDs data table format or from a STORET database, an EQUIS database, and NOAA's Query Manager database via a FIELDs-defined data table export create by these database developers. If a user has field names or types that do not match the FIELDs-defined data table format, an interactive

GUI allows users to match their field names with the FIELDS-required names. The query options in the Database Query module include creating 3D datasets and 2D datasets. For the latter, a user may create maximum values per location or depth-weighted average datasets. The latter dataset allows a user to use 3D data by creating 2D data layers. The resulting queried data values can be used in the Human Health Risk or Ecological Risk Assessment modules. Each module meets U.S. EPA guidelines (RAGS and ERAGS) for risk assessment. In addition, the queried data can be modeled (interpolated) to create estimates at unsampled locations using Dr. Dave Watson's Natural Neighbor algorithm or ArcView's Inverse Distance Weighting (IDW) algorithm. The FIELDS Tools also include a cross validation routine that generates root mean square errors (RMSE) of estimation for permutations of the IDW parameters' number of neighbors and power. The interpolated values can be used to estimate the mass of contaminant (e.g., pounds of PCB) and the volume of contaminated material (e.g., sediment > 10 ppm) using the Mass/Volume module. Finally, the FIELDS Tools includes a Remediation module that allows users to determine areas to remediate in order to meet a clean-up goal by remediation unit (called block-based remediation) or for the entire site (i.e., to meet an average concentration value for an entire area). Figure 2 shows the FIELDS extensions in ArcView and the FIELDS query results of the 0-15 cm layer created using depth-weighted averaging.

The FIELDS Team has also developed a stand-alone 3D Viewer software called F/S Plus. It is a fully-integrated tool that displays and allows analyses of 2D and 3D data. F/S Plus can perform the following functions:

- import and view point, line, polygon, and grid files
- execute three different interpolation methods: Inverse Distance Weighting (IDW), Natural Neighbor (NN), and Kriging
- view resulting 2D and 3D grids as "blocks" or "isosurfaces"
- volume estimation, interpolation error estimation, and grid statistics
- clipping (top, bottom, and lateral)
- 3D-slicing and export to ArcView
- cross-section creation
- polygon-builder tool
- viewing functions (e.g., zoom, transparency, point size, mirror)

Figure 3 demonstrates the F/S Plus "look" with data points and a 3D-interpolated plume of Radium contamination.

The FIELDS Tools forms the foundation for a system that provides data analysis and interpretation for environmental decision-making. The results allow project managers to evaluate the extent of contamination and hot spot sizes, estimate health risks, prioritize site goals, and weigh potential actions.

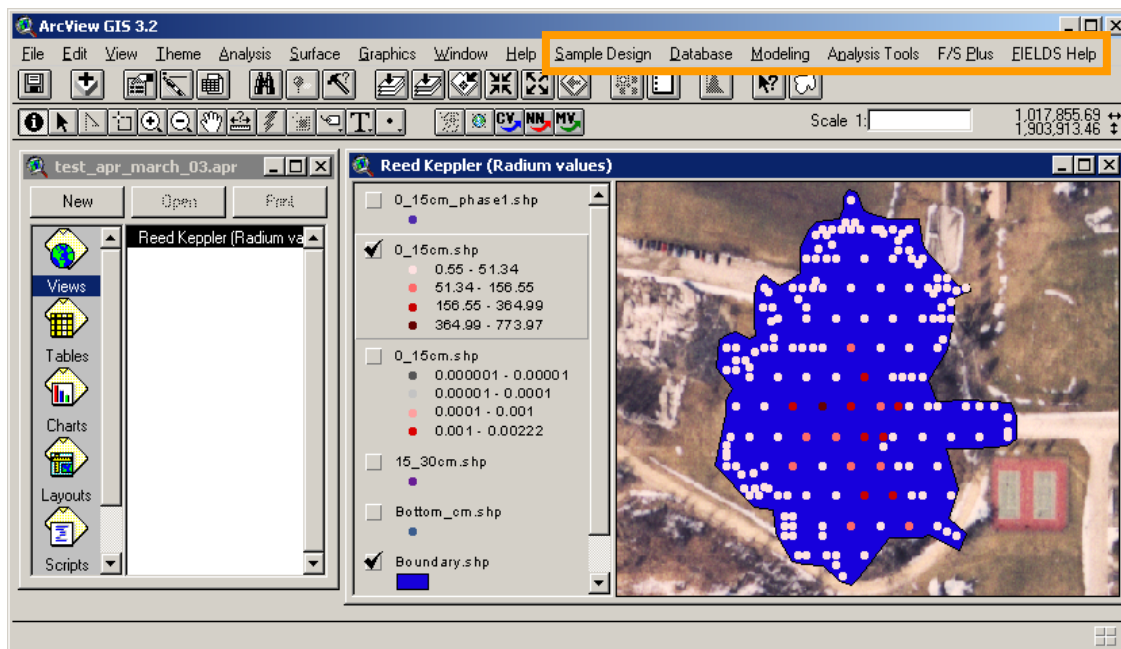


Figure 2

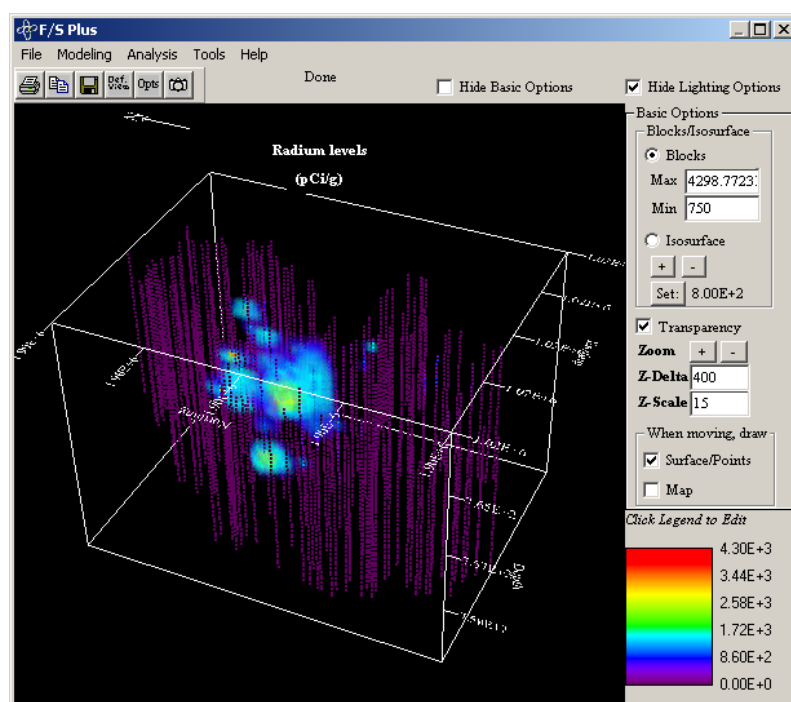


Figure 3

### Integration of VSP and FIELD5 Software

The VSP and FIELD5 development teams have been sharing software development ideas over the past three years. Both VSP and FIELD5 teams were interested in expanding their software capabilities but realized some of the planned enhancements may be duplicative. For instance, FIELD5 developers were interested in expanding their sampling design options whereas VSP developers were interested in expanding their ArcView compatibility and geostatistical options.

Support from EPA and DOE provided an opportunity to explore how these tools might be integrated to provide a seamless toolkit for potential users.

In March 2003, VSP and FIELDS rolled out the first integrated package. Now, with FIELDS version 3.5, VSP can be called up directly within the FIELDS ArcView environment. Maps are automatically passed between VSP and FIELDS and the sample coordinates generated in VSP are passed back into FIELDS as ArcView Shapefiles (\*.shp). The VSP report generator is also automatically saved to a file when leaving VSP and returning to FIELDS. Although not all VSP modules are integrated with FIELDS, several of the most prevalent sampling goals are functional. Further work will be required to fully integrate the two packages, including the UXO and adaptive sampling modules.

This integration activity has exceeded our expectations for how we might connect these two software packages. We are avoiding unnecessary duplication of effort and building trusting relationships between the team members. Future integration activities are planned to support integration between FIELDS, SADA, FORMS II Lite and VSP and to develop a toolkit that can be accessed inter-changeably by users. We hope to provide software that is powerful, versatile, and most of all understandable.

# **The Challenge of Quality Assurance for Emission Flux Measurements of Large Area Sources by Optical Remote Sensing**

Shirley J. Wasson, Mail Code E343-03  
USEPA, National Risk Management Research Laboratory  
Air Pollution Prevention and Control Division  
and  
Robert S. Wright, RTI International

*The regulatory arm of the Agency is interested in monitoring the emissions flux of contaminant gases from large area sources. Such sources include large livestock operations, coal mines, water treatment plants, and municipal landfills. Concentrations are measured by an optical remote sensing (ORS) device, then calculations involving concentrations, wind speed, and wind direction are performed to reconstruct the plume that provides estimates of the emissions flux.*

*This presentation will concentrate on the open path Fourier transform infrared (OPFTIR) spectrometer ORS method for concentration measurements. Its advantages are that an EPA compendium method is available to provide guidance and that it can measure many compounds simultaneously without a large number of point samplers or analyzers. Its disadvantages are that it is expensive, it requires a highly trained crew, interferences must be accounted for during the concentration calculations, and it is slow compared to rapidly changing wind conditions.*

*Traditionally, dispersion modeling has been used to provide plume reconstruction, but computed tomography (CT) has gained popularity in the last few years. Path integrated concentrations (PICs) are determined using multiple optical beam paths in the vertical and/or horizontal planes. Then a mathematical function is fitted to the measured PICs, and the spatial distribution of concentrations is generated for a plane perpendicular to the direction of the wind moving across the area source or horizontal above the source. Estimates of the emission flux are determined by integrating the product of the calculated concentrations and wind speeds over the plane.*

*The quality assurance challenges arise because no standard method exists for the complete process. Although EPA has Compendium Method TO-16 for OPFTIR, project personnel are required to choose between several options without adequate guidance. Such choices include the ORS concentration measurement device, the CT calculation methods required to arrive at the spatial distribution, and the mathematical methods used to reconstruct the plume and the vertical wind field and to calculate the emission flux. Defensible estimates of the uncertainty of the final emission flux have not yet been developed. A data validation procedure is needed for the entire measurement and calculation process. Auditors are challenged to configure an adequate performance evaluation standard that is representative of a large area source.*

*This presentation will examine the critical decisions required to perform adequate OPFTIR measurements with plume reconstruction by CT and how each challenge may be met.*

## **Introduction**

Optical remote sensing (ORS) measurements are performed over large area sources to determine emission fluxes of environmental contaminants. The challenge is to assure quality for such measurement projects (Russwurm and Childers 1997). Basic considerations for ORS measurements include:

- selecting the ORS device, performing pre-field deployment checks
- selecting and checking the geographical and meteorological measuring instruments
- siting the device for background and contaminant measurements
- creating synthetic background spectra, selecting reference spectra, identifying and quantifying target contaminants and interfering species
- determining mathematical algorithms to calculate emissions fluxes.

## **The ORS device**

Differential absorption light detection and ranging (LIDAR), tunable diode lasers, differential optical absorption spectroscopy (DOAS), and open path Fourier transform infrared (OPFTIR) have been used for ORS. For several reasons, this presentation will concentrate on the OPFTIR technique. EPA (U.S. EPA 1999, Russwurm et al. 1996) and ASTM (ASTM 1998, ASTM 2002) have issued standard guidance for its use, it has been used extensively, and it can measure many contaminants simultaneously.

An FTIR consists of an IR source, an interferometer, focusing optics, a detector, electronics, and a computer. The principle of measurement is that the system produces an interferogram containing information on the concentrations of the chemicals in the open air path that absorb energy in the IR portion of the electromagnetic spectrum. The Fourier transform of the interferogram is the original spectrum of intensity as a function of wavenumber ( $\text{cm}^{-1}$ ). One challenge is that, in addition to the organic pollutants of interest, the spectrum also prominently features interfering species including water, carbon dioxide, carbon monoxide, nitrous oxide, methane, and deuterated water.

In a monostatic type FTIR, the IR source sends collimated IR radiation across the site to a retroreflector which returns it through receiving optics to a detector located near the source. The optical pathlength is thus twice the physical pathlength. In a bistatic system, the IR source is at one end and the detector at the other. The beam may traverse the interferometer either before or after it leaves the source but before it is detected.

The resolution of the system must be sufficient to separate the absorbance spectra of the target analytes from interfering species. The required resolution is specific to the target analytes and the interference of water in their spectral areas. The data are stored as interferograms that are later deconvoluted into absorbance spectra; i.e., intensity as a function of wavenumber.

## **Selecting and checking instruments: DQOs and DQIs**

One key to collecting optimal data is to determine written data quality objectives (DQOs) based on the objectives of the project. A typical objective is to improve source emission data supporting AP-42, a compilation of air pollutant emission factors maintained by the Office of Air Quality Planning and Standards (OAQPS) at EPA. OAQPS uses AP-42 to define pollutant emission levels as a function of industrial production levels, thus generally requiring Category 2 quality assurance (QA) at the Office of Research and Development (ORD) project level. Given the use of the data, emissions are quantified at the levels consistent with the limits of the instruments.

Thoroughly recorded checks of the FTIR before field deployment and similar checks at least twice daily in the field are critical to good data. Table 1 lists the properties, procedures, and limits for these checks. Data quality indicators (DQIs) are measured for each critical measurement. Table 2 provides a typical table of DQIs based on DQOs for the theodolite, anemometer, wind vane, the relative humidity sensor, thermistor, and barometer. Precision and accuracy checks against a standard are performed and the results recorded. Quality control (QC) checks are performed during data collection according to written operating procedures (OPs). Table 3 shows additional required field QC checks for optimal data.

Table 1. FTIR checks before field deployment and during field data collection (twice per day)

Property	Procedure	Limit
Electronic noise	Record signal with detector blocked	<0.25% of signal
Minimum pathlength for detector saturation	Check the spectrum below the detector cutoff frequency	Flat and at the baseline <sup>1</sup>
Linearity	Determine change in absorbance with changes in concentration	Concentration versus absorbance is a straight line, but nonlinear relationships can be analyzed.
Monostatic: stray light Bistatic: ambient black body	Collect a spectrum away from the reflector. Collect a spectrum with the IR source off.	No limits set, but must be known
Signal strength with distance	Starting at saturation distance, move the reflector or source and determine the signal, diminishes as square of distance	Minimum-saturation distance Maximum-stray light/ambient radiation
Random baseline noise	Difference in successive absorbance spectra	Flat line

<sup>1</sup>Particles may raise the baseline.

## Siting

Severe challenges to good data start with the site. Typical ORS measurements traverse large open spaces such as containment lagoons in large animal breeding operations, municipal water treatment settling ponds, municipal landfills, and surfaces of coal strip-mining operations. EPA has provided guidance (Federal Register 1994) for choosing the path. The optimal site provides a reasonably level surface, clear weather conditions, a steady wind perpendicular to the optical path, and no obstacles.

The optical path is typically sited on the downwind side of the area source with the OPFTIR

located at one end of the path and the retroreflectors or IR sources located at the other end. The monostatic FTIR, mounted on a computer-driven scanning device, is directed toward the retroreflectors. It scans for a short time at each retroreflector position in a predetermined spatial and temporal pattern. The retroreflectors are located on stands a few feet from the ground for a radial scan pattern that is appropriate to measure a horizontal plane above the plume source. If a vertical component is desired, some of the retroreflectors are elevated, typically on a large scissors jack several meters in height. Background measurements require a second OPFTIR sited upwind of the area source. The choice of scan pattern depends upon project objectives.

Table 2. DQIs for Critical Measurements in Field

Measurement	Instrument	Precision	Accuracy	Standard	Range
Pathlength	Theodolite	$\leq 1\%$	$\pm 0.1$ m	NIST <sup>1</sup> traceable length measure	0 to 200 m or higher
Wind speed	Anemometer	$\leq 5\%$	$\pm 5\%$ of scale	Wind tunnel	0 to 30 km/h
Wind direction	Wind vane	$\leq 5^\circ$	$\pm 5^\circ$	Magnetic north pole	$45^\circ$ to $135^\circ$
Relative humidity	Sensor	$\leq 5\%$	$\pm 5\%$	Salt solutions	Humidity range during project
Temperature	Thermistor	$\leq 1^\circ$	$1^\circ\text{C}$	NIST traceable thermometer	Temperature range during project
Barometric pressure	Barometer	$\leq 1\%$	1 mm Hg	Compare with NOAA <sup>2</sup>	Barometric pressure range of project

<sup>1</sup>NIST = National Institute of Standards and Technology

<sup>2</sup>NOAA = National Oceanic and Aeronautical Administration

Table 3. Additional field checks, at least twice per day

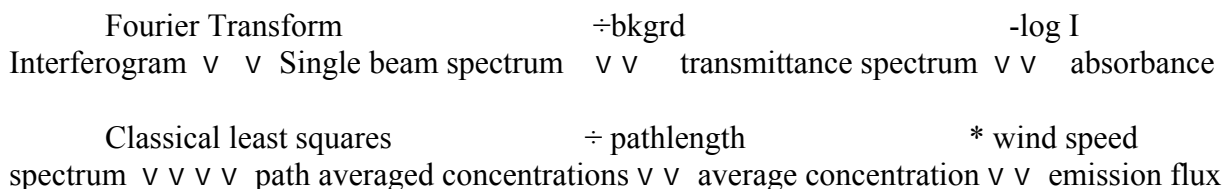
Property	Procedure	Limit
Return response.	Measure signal strength at chosen pathlength. Note weather conditions	Acceptable value: (% of saturation) 10 to 30%, monostatic configuration 85 to 90%, bistatic configuration
Linearity of response	Check interferogram Check single beam spectrum.	A mirror image; baseline is straight with no dips and no hills. The opaque areas (strong water and carbon dioxide absorption) are flat and zero.
Changes in resolution.	Check for wavenumber shifts ( $\text{cm}^{-1}$ )	Water has a singlet @ $1014\text{ cm}^{-1}$ , and deuterated water (HDO) occurs @ $2720\text{ cm}^{-1}$ .
Background spectrum	Various procedures.	No absorption bands due to target analytes present. Shape matches single-beam field spectra
N <sub>2</sub> O	Check concentration against known amount in atmosphere	N <sub>2</sub> O is 310 ppb at $2155$ to $2225\text{ cm}^{-1}$ .
H <sub>2</sub> O	Check concentration against independent measure	H <sub>2</sub> O partial pressure in air is calculated from relative humidity and temperature.
Target analytes	Check concentrations against reference spectra.	Absorbance versus concentration is straight line with origin at zero. Nonlinear relationships can also be analyzed.

Meteorological conditions are important. Snow and fog scatter the signal. The wind speed and direction should remain steady for extended periods to allow the signal-to-noise ratio to be improved by the addition of consecutive scans of the OPFTIR. Decisions regarding resolution, pathlength, scanning times, vertical height, and spatial configuration will determine the minimum detection limits, accuracy, and precision of the measurements consistent with the DQOs of the project.

### Analyzing the data

Spectral data coordinated with weather conditions are saved to data storage devices in temporally identified files. Calculations proceed according to the flow chart in Figure 1 using commercial software supplied with the FTIR. First the interferograms may be mathematically optimized by zero-filling and apodization. Then they are converted to single beam spectra for each sampling period and corrected for stray light or blackbody radiation. Next, background spectra are prepared, chosen from parts of the spectrum in the background measurements where the contaminants of interest appear in the field spectra. Background spectra are free of intensities from target contaminants, have the same general shape as the field spectra, and are measured over the same pathlength as the field spectra. Sample spectra are ratioed to the background spectra to generate transmittance spectra. Taking the negative logarithm of the transmittance produces the absorbance spectra that are used for the final data analysis.

Figure 1. Calculation steps to emission flux



Since water is always present in the atmosphere, it must be accounted for in the sample spectra during analysis. For this purpose a water vapor reference spectrum is generated, either from field data or taken from a high quality source such as the HITRAN database (University of South Florida 1993). The primary concern is that the water reference spectrum is void of the analyte of interest.

Reference spectra for identification and quantification of unknowns must be available for the analysis. Synthetic spectra of the atmospheric gases (CO<sub>2</sub>, CO, etc) can be generated from the HITRAN database. National Institute of Standards and Technology (NIST) standard reference IR spectra are available for 23 organic compounds. For others, commercial spectral libraries are available, but there is no independent organization responsible for validating the accuracy of these spectra. The spectral resolution of the synthetic spectra must match the resolution of the sample spectra, otherwise systematic bias in target analyte concentrations will result.

Analysis proceeds by selecting appropriate small spectral regions for the target unknowns.

Ideally the target analyte has high absorptivity in the region, and interferences can be identified and accounted for. Classical least squares (CLS) analysis is a preferred method of analysis when the concentrations of several target gases are to be determined and several interfering species are present. CLS finds the linear combination of reference spectra that minimizes the sum of squared differences between the field spectra and the linear combination of reference spectra. Since the reference spectra are added together in CLS, spectral features in sample spectra do not need to be resolved. All species that have absorption features in the spectral region must be included. Contributors to the residuals include possible nonlinearity between absorbance and concentration, detector nonlinearities, inadequate spectral resolution, optically dense absorption bands, and poor baseline modeling.

The outcome is path-averaged concentrations of the target analytes. Dividing by the pathlength gives the average concentration over the path for the sampling time period. Sequential time periods are analyzed to determine the sustainability of the concentrations in the plume.

### **Emission Fluxes**

Standard guidance for OPFTIR monitoring provides average concentration data over large open sources. To produce emission fluxes, these data are integrated with the wind data. Two current methods to calculate emission fluxes are wind dispersion models and computed tomography (CT). CT has been successfully compared to The Industrial Source Complex–Short Term (ISCST) model and the American Meteorological Society/EPA Regulatory Model Improvement Committee (AERMOD) model (Piper 1999). The CT maps were found to track the impact of changing wind direction better than the models.

CT has been applied by different researchers using a variety of functions to map the pollution field. It is not yet known if the emission flux predictions of different functions and CT methods agree. A desirable function minimizes the differences between calculated and measured concentration values. As the function is iteratively fit to calculated values of concentration, goodness of fit can be measured by the concordance correlation factor (CCF). A bivariate Gaussian function is a Smooth Basis Minimization Function useful for this purpose (Hashmonay 1999). The function has six independent unknown variables requiring six independent beam path measurements to determine the unknowns. The bivariate Gaussian function conserves volume, not shape. Therefore the tomographic map is only representative of the shape of the plume.

One disadvantage of measuring air contaminants by FTIR is that it may be slow compared to changes in wind speed and direction. Comparing the stability of successive values of the average flux is a measure of the variability of the results. Concentrations of several successive measuring periods may need to be added to bring the value above the minimum detection limit (MDL). The criteria for co-adding scans should be predetermined. Only those data meeting that criterion should be reported.

### **Validation of the overall method**

Several practitioners have attempted validation studies in the laboratory using known concentration of pollutants in confined spaces. Success has been limited due to several factors. The confining wall of the space changes the characteristics of the measurement. The background

spectrum does not contain the interferences of the atmosphere such as changing water vapor concentrations or unidentified interferences. The ideal situation would be to release an internal standard gas with the same characteristics as the pollutant targets in the same configuration as the unknown source. The primary difficulty is that most candidate gases are heavier than target pollutants and do not disperse similarly. Also what configuration will represent an area source?

Practitioners of ORS-CT have attempted to validate the method (Hashmonay 2001) using simulated area sources in the field. Nitrous oxide was released at a known rate from soaker hoses arranged in an H-pattern in a field. Recovery was 66% for unstable wind conditions, and for more stable conditions, 90%. Work continues to standardize the method.

## Conclusions

Optical remote sensing is well established as a viable analysis method for providing path-integrated concentrations of large area sources of pollutants. Quality assurance practices and indicators are available to assess the precision and accuracy of the measurements. Calculation of emission flux by CT using these concentrations is still in the development stages with validation of the overall method by better simulation of area sources under a variety of field conditions the ultimate goal.

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# How to Get Good Science from a Cement Mixer: Measuring the Precision and Accuracy of EPA Method 1668A

V.A. Pretti New York State Department of Environmental Conservation

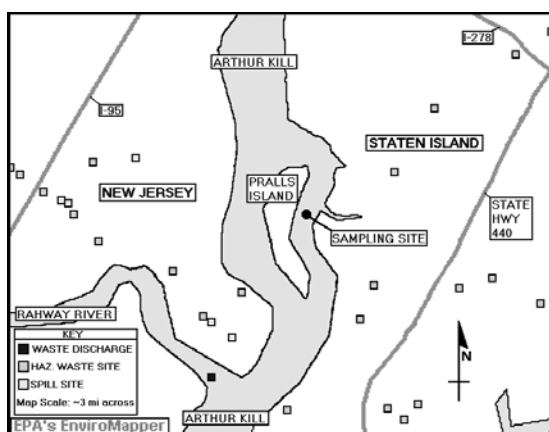
*One of the main goals of the NYS Department of Environmental Conservation's Division of Water (NYSDEC DOW) is to assess the status and trends of water quality in the NY/NJ Harbor and Estuary and to understand the natural and anthropogenic factors that affect water-quality conditions. The DOW has established high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) as a standard to measure dioxins/furans, chlorinated pesticides, polychlorinated biphenyls, and polynuclear aromatic hydrocarbons, in spite of the current EPA methods for HRGC/HRMS not being fully validated. Previous analytical work associated with the NY/NJ Harbor Pre-Dredge project suggested that a broad range of organic pollutants existed in the Arthur Kill on the western edge of Staten Island. On May 27, 1998, NYSDEC conducted sampling of sediment in the Arthur Kill. A series of ponars were extracted in the Kill on the east side of Pralls Island. Approximately 38 liters of sediment were homogenized, transferred to sample vials in the field, and then frozen. To fulfill our study objectives, we used a modified version of EPA Method 1668A and treated the composited sediment as a long-term Ongoing Precision and Recovery (OPR) study in the harbor. Aliquots were routinely sent to four separate, contracted laboratories for analysis of organic pollutants from Spring 1998 through Summer 2001. In this study, we focus on polychlorinated biphenyls (PCBs). Analytical results are used to compare the accuracy and precision of method 1668A to identify and quantify the 209 PCB congeners. Uncorrected PCB concentrations vary widely among the labs on a congener-by-congener basis; however, the precision on a total PCB basis and by homologue is less than 30% RSD. The method is also successful in determining unambiguous results for the World Health Organization (WHO) Toxic PCBs. Congener-by-congener shifts in the relative importance of total, homologue, and toxic PCB results appear to be only second-order effects on overall data quality. Congener selectivity is in part due to the relative contributions of individual laboratory GC temperature programs, co-elution patterns, and number and type of labeled standards used.*

## INTRODUCTION

The New York/New Jersey Harbor system, a vital center of commerce for the East coast and the nation, requires periodic dredging in order to increase channel depths for the safe passage of ships and barges (1). Historically, spoils from NY/NJ Harbor dredging activities were disposed of at sea, but in 1992 the Environmental Protection Agency (EPA) enacted stricter regulations regarding ocean disposal. In 1996 the federal government mandated the closure of the Mud Dump Site, the ocean disposal site used by the NY/NJ Port Authority for dredge spoils. After September 1997, the only material deposited at the site could be pristine Category 1 material that makes up only 14% of the material to be dredged in the coming years from the harbor.

In response to the federal action, New York State Department of Environmental Conservation

(NYSDEC) became involved in a bi-state Contamination Assessment and Reduction Project (CARP) with various agencies from NY and NJ. The focus of CARP is to understand the fate and transport of ubiquitous pollutants: metals, dioxins/furans, polychlorinated biphenyls, polynuclear aromatic hydrocarbons, and chlorinated pesticides for example, discharged into the Harbor (2-4). NYSDEC has established high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) as a standard method to measure organic contaminants. This method is extremely sensitive, providing results in the 5–500 ng/kg range, in comparison to the low resolution method 8082 (5), providing results in the 160–800 ng/kg range. At the present time, HRMS methods are costly, time consuming, not fully validated by EPA, and lack acceptance by a consortium of industrial organizations because of its limited inter-laboratory validation (6).



**Figure 1 Location of sediment sampling site in the Arthur Kill (indicated by a solid black dot).**

In response to the doubts, NYSDEC decided that an Ongoing Precision and Recovery (OPR) study of Harbor sediments would demonstrate the usefulness and validity of HRGC/HRMS. In 1998, NYS DEC collected a large volume of contaminated sediment in the Arthur Kill near Pralls Island (Figure 1), which is surrounded by oil tank fields and sanitary landfills. In this paper, we focus on polychlorinated biphenyl (PCB) results from 45 separate analyses of the homogenized OPR sediment by HRGC/HRMS. We use the results of the OPR study to compare the accuracy and precision of method HRMS-1 to identify and quantify PCBs on a total, homologue, congener-by-congener, and dioxin-equivalent toxicity basis. In addition, we compare GC parameter settings, co-elution patterns, method blanks, detection limits, and labeled compounds utilized by the analytical labs. The impact of these factors is considered when comparing inter-laboratory and intra-laboratory PCB concentrations.

## MATERIALS AND METHODS

On May 27, 1998, NYSDEC conducted sampling in the Arthur Kill. A series of standard ponars were collected in the Kill on the east side of Pralls Island (Figure 1). Sampling was accomplished from a NYSDEC pontoon boat in approximately 1 m of water. The ponar removed the top 10-12

cm of sediments. Approximately 38 liters of sediment were composited and homogenized for 15 minutes in a plastic cement mixer and immediately transferred to decontaminated 40-mL vials using a pre-cleaned stainless steel syringe in the field. The sample vials were then frozen at a secure location in the DEC central office in Albany. Contamination was kept to a minimum by positioning the boat's motor away from the sampling site and pre-rinsing the sampling equipment with the ambient waters. Since the samples were taken from the same site and mixer, it was unnecessary to decontaminate between sample transfers.

Aliquots were routinely sent to four separate, contracted laboratories, along with other CARP samples, for analysis of primary organic pollutants. Between Spring 1998 and Summer 2001, 45 replicate samples were shipped to the contracted analytical labs with samples from other CARP monitoring sites. The samples were labeled, OPR, and were not considered blind quality control items. The analytical labs used NYS DEC HRMS-1 method (7), that is partly based on EPA Method 1668A (8) and technical literature (9-11), for the extraction, concentration, cleanup and determination of PCBs. The major divergences from method 1668A included using a single column, preferably an SPB-octyl column that resolves all the toxic congeners except for IUPAC 156 and 157, and a final extract volume of 100  $\mu$ L instead of 20  $\mu$ L. Method HRMS-1 was similar to method 1668A in that it is a performance-based method.

NYSDEC recommended that a 10-g portion (dry weight) of sediment sample be used, but accepted the smallest representative amount ( $\geq 1$  g). The homogenized aliquot of each sample was spiked with a solution of  $^{13}\text{C}$ -labeled PCB congeners. The labeled congeners were chosen to represent the native congeners of highest toxicity and to match the 10 levels of chlorination (LOC) present in the 209 PCB congeners (12). In addition to the sediment sample itself, two separate aliquots of sodium sulfate ( $\text{NaSO}_4$ ) were weighed to  $\sim 10$  g and spiked with the same labeled compounds as the sample. One of the  $\text{NaSO}_4$ - aliquots was spiked with a select number of native PCBs to serve as the spiked blank while the other aliquot served as the method blank. Sediment samples were extracted using a Soxhlet/Dean-Stark extractor with toluene as the extraction solvent and then cleaned up to eliminate interferants. Cleanup varied by lab and included the use of any or all of the following procedures: silica gel, Carbowax/Celite, gel permeation chromatography, and high performance liquid chromatography. The final extract volume was set to 100  $\mu$ L in nonane, and injection internal standards were added.

Samples and standards were analyzed by HRGC/HRMS. GC conditions and columns used by the labs are summarized in Table 1. At least 5 standards, ranging in concentration from 1.0 to 2000 ng/ml, were required for initial calibration; however, some labs initially calibrated with a 0.2 ng/ml standard. Daily calibration was confirmed with a 50-ng/ml standard.

## RESULTS AND DISCUSSION

The four laboratories achieved excellent precision for the quantification of total PCBs and PCBs on a homologue basis. Total PCB concentration for the 45 samples average  $1562 \pm 343$   $\mu\text{g/kg}$

dw (Figure 2a). The average relative standard deviation (RSD) for total PCB and PCB homologue results is  $25 \pm 8\%$  and  $30 \pm 7\%$ , respectively. Lab A has the lowest total PCB RSD (11%) and homologue RSD (15%). At 29%, Lab S has the highest total PCB RSD. Lab W has the highest homologue RSD at 34%. It is difficult to assess a bias for the OPR sediment sample because the true PCB concentration in the sample is unknown. However, the PCB levels found are consistent with other data sets for PCBs in sediment from the Lower Hudson River and NY Harbor (3, 13). When the per lab average concentrations are compared to the total average PCB concentrations of the four labs minus the average of the lab of concern, the bias for total PCBs and homologue results is  $107 \pm 29\%$  and  $106 \pm 27\%$ , respectively.

**Table 1. HRGC/HRMS systems used to analyze PCBs in sediments of the Arthur Kill.**

<b>Laboratory</b>	<b>A</b>	<b>P</b>	<b>S</b>	<b>W</b>
<u>Column Type Manufacturer</u>	SPB-octyl <sup>a</sup>	SPB-octyl	DB-5 <sup>c</sup>	RTX-5SILMS
<u>Carrier Gas</u>	He	He	He	He
Pressure (psi)	29	60 at tank	20	programmed
Flow (cm/s)	67	EPC <sup>b</sup>	1.4	25
Flow Temp (°C)	75	N/A	190	100
<u>Temp Program</u>				
Start (°C)	75	100	120 <sup>d</sup>	100
Hold (min)	2.0	2.5	1	1.0
Ramp 1 (°/min)	15.0	10.0	6	35.0
Stop (°C)	150	200	320	150
Ramp 2 (°/min)	2.5	2.0	N/A	1
Stop (°C)	275	270	N/A	200
Hold (min)	4.0	2.5	1.75	0 <sup>e</sup>
<u>Congener Selectivity</u>	125	133	120	149
<u>Max Oven Temp (°C)</u>	280	270	320	290
<u>Injector Temp (°C)</u>	270	250	270	285
<u>PCB 209 (min)</u>	55	46:20	36:10	78
<u>Model</u>	Autospec Ultima (VG-70)	Autospec X (VG)	Micromass TYPE9924B	Kratos Concept 1H

<sup>a</sup> Lab A also used an IP deactivated guard column by Restek.

<sup>b</sup> Lab P used an electronic pressure controller (EPC) set at a constant flow (1mL/min).

<sup>c</sup> Lab S used an SPB-octyl column in 2000. The parameters varied as follows: column (30m,0.25mm,0.25µm), temp program (150°C,2min,10°/min,200°C,2°/min,274°C,1min), max oven temp (274°C), and PCB 209 (45min).

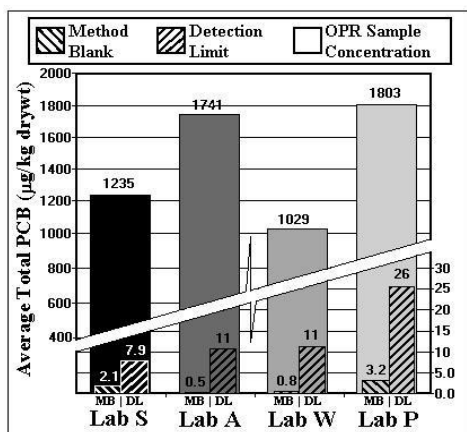
<sup>d</sup> Lab S used an adjusted temp program in 2001 (150°C,1min,3°/min,270°C,20°/min,320°C,1.50min) and PCB 209 (46min).

<sup>e</sup> Lab W used a third ramp, stop and hold in the temp program of 3°/min, 290°C, and 0min, respectively.

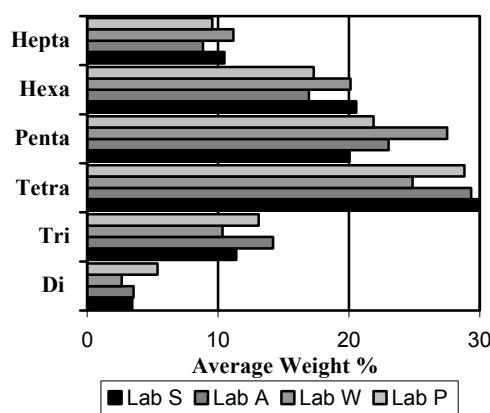
Determination of individual congener concentrations is much more challenging than measuring the total PCB or homologue concentrations. The average congener RSD for the OPR data set is  $138 \pm 147\%$ . The intra-laboratory average congener RSD ranges from 41% to 64%. These results show significant differences in the determination of individual congener concentrations among labs and fairly consistent precision within an individual lab to identify and quantitate the same congeners. Larsen (1995) contributed the complexity of individual congener identification and quantification to differences in GC column type, temperature program, and carrier gas type (14). To achieve separation of PCBs, weak dispersion forces are necessary, as well as, increasing temperatures to increase the partial pressure of the PCB congener and shift the congener towards its gas phase at a rapidly increasing rate that increases its selectivity. The SPB-octyl and DB-5

columns are capable of resolving IUPAC congeners 34/23 and 187/182, and congeners 156/157 elute (7). Lab W, using an RTX-5SILMS column, was the only lab unable to resolve 187/182, but was capable of separating 156/157. Congener selectivity of the labs is listed in Table 1. The variations in selectivity between lab A and P, who both used the SPB-octyl column, can be attributed to variations in temperature programs (Table 1). Congener co-elution patterns also have an impact on method precision. Among the four laboratory data sets, 80 congeners were always eluted as unique peaks. The average per congener RSD is reduced from 138% to 93% for these 80 congeners; therefore, improving the data quality.

**Figure 2 Variations in averages for the OPR sample, method blank, detection level, and homologue results. In Figure 2a, values above the rectangles correspond to average total results. Note the change in the scale of the y-axis. Figure 2b gives the average weight % of Cl-homologues. Mono-, octa-, nona-, and deca-homologues are not included because the average weight %'s are < 5 weight %.**



2a



2b

The average RSD of the World Health Organization (WHO) Toxics is 51%. It is apparent that the inter-laboratory precision of the WHO Toxics is more reliable and fairly precise. Average PCB concentrations for the toxic PCBs range from 53 µg/kg dw for IUPAC 169 to 45,000 µg/kg dw for IUPAC 118. About 86% of the sediment toxicity is attributed to the coplanar PCBs with IUPAC numbers of 118, 126 and 156. PCB118 has a significant impact on toxic equivalency (TEQ), since its average concentration is very high, even though its assigned toxic equivalence factor (TEF) is  $10^4$  times less than 2378-TCDD (12). PCB126 has a substantial impact on the TEQ based on its high TEF (0.1) for mammals, but its average concentration in the sediment is very low (169 µg/kg dw). In all, the toxins contribute only 8-wt % to the total PCB.

The EPA believes that backgrounds of many of the PCB congeners are difficult to eliminate, and that these backgrounds can interfere with the determination of PCBs in environmental samples (8). The laboratories used method blanks (MBs) to monitor the effects of contamination on PCB results. On average, the total PCB measured in the OPR samples is 1600 times larger than the

total PCB measured in the MBs (Figure 2a). The average per congener concentration of the data set is ~4300 times greater than the average per congener MB concentration. Therefore, MB results have more influence on the total results rather than on the congener results, but overall, the OPR PCB results are not affected by laboratory contamination. Additionally, average DLs are significantly below the OPR sample results and have minimal influence on variations in PCB concentrations (Figure 2a).

The number and type of labeled analogs used appear to influence the high inter-laboratory variability of the 209 congeners. Twenty-seven labeled PCB compounds are used in Method 1668A to monitor system performance and to quantify specific PCB congeners. In this study, the laboratories use a range of different labeled congeners. The minimum number of labeled analogs used by any one lab, at any given time, was 15 by lab S. Lab A used as many as 30 labeled compounds during the 3-year study. The labeled congeners have a positive influence on the overall precision of the homologue results. The predominant homologue series (tetra, penta, and hexa) consist of the most number of PCB isomers, contribute 70-wt % to the Total PCB (Figure 2b), are monitored, in most cases, by the largest number of labeled congeners (6, 5, and 5, respectively), and are consistent with Aroclor trends in the Upper Hudson River, of which the Arthur Kill is an extension (15). Nine labeled PCB congeners (IUPAC 3L, 15L, 77L, 105L, 118L, 156L, 167L, 169L, and 209L) were consistently used by all the labs. The average recovery for the 9 labeled compounds is  $67 \pm 10\%$ . When the native PCBs are quantified against the 9 labeled congeners, the average per congener RSD is 39% for the natives, ~4 times lower than the RSD for all 209 congeners. The impact of the labeled congeners on the average congener RSD suggests that the congener RSD would improve as the number of labeled congeners used increases.

## CONCLUSIONS

We provided a carefully reviewed, long-term, inter-laboratory validation study on a realistic sample. In response to the recent doubts made by a group of industries on the suitability of method 1668 and 1668A, the four laboratories successfully met the requirements of the HRMS-1 method to provide precise data for total PCBs, homologue PCBs, and to a certain extent Toxic PCB congeners. The intra-laboratory congener precision was considerably better than the precision of individual congener concentrations among the laboratories. On a whole, the congener precision appeared to have minimal effect on the precision of total and homologue PCB quantification within a lab and among the labs. Poor congener selectivity was in part due to the temperature program settings, GC column, and number and type of labeled congeners used by the individual laboratories. NYSDEC Method HRMS-1 offered data quality improvements over the Aroclor and congener analysis by Method 8082. Congener detection limits for method HRMS-1 were in the subpart-per-trillion level, in comparison to the low-resolution method 8082. We estimated that method HRMS-1 was capable of analyzing the OPR sediment with a bias of  $107 \pm 29\%$  and  $106 \pm 27\%$  for total PCBs and homologue results, respectively. The main downfall of the relatively new methods, HRMS-1 and 1668A, is the price of analysis. As the number of analytical labs performing the HRMS analysis expand and become more competitive, the price of analysis should drop.

## ACKNOWLEDGEMENTS

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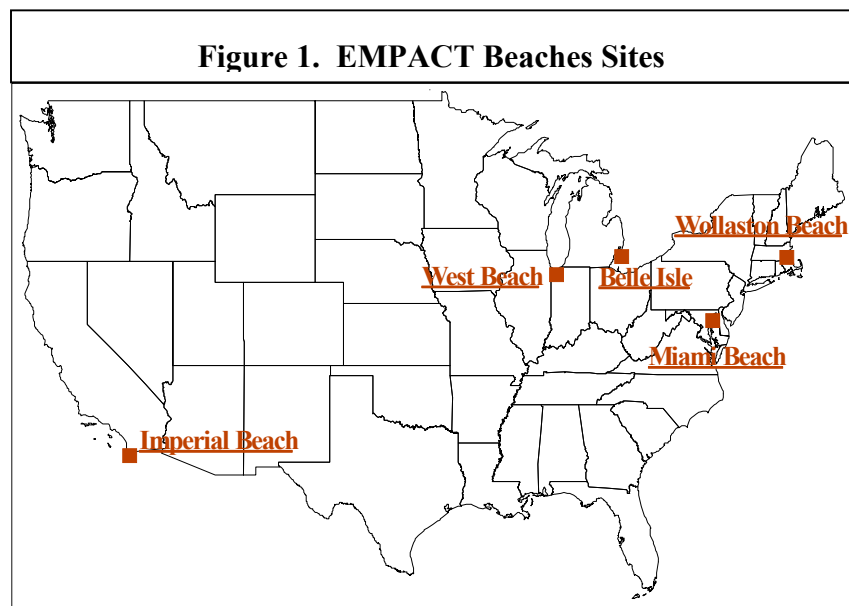
## Information Management for a Large Scale, Multi-Site Research Project

John Martinson<sup>1</sup>, Daniel Lewis,<sup>2</sup> Larry J. Wymer<sup>1</sup>, Kristen P. Brenner<sup>1</sup>, and Sherie L. Brown<sup>1</sup>  
<sup>1</sup>National Exposure Research Laboratory (NERL), Office for Research and Development (ORD),  
U.S. Environmental Protection Agency, <sup>2</sup>OAO Corporation

*The EMPACT Beaches Project was a field survey managed out of EPA's National Exposure Research Laboratory in Cincinnati. Water samples were taken from beaches and tested for fecal indicator bacteria. A variety of ancillary field data were also collected. The study, conducted during July and August of 2000, resulted in close to 500,000 pieces of information being recorded from five beaches scattered across the country. This paper focuses on the data management aspects of the project, explaining how the project data was channeled in a continual, orderly flow that was funneled into a single Microsoft Access 2000 database. The unique approach employed resulted in a verified database being available in December 2000. Thoughts on why the effort proved so successful are provided.*

### Study Description

Beaches for this study were in or near partner cities in the Environmental Monitoring for Public Access and Community Tracking (EMPACT) grants program. The five beaches in the study are shown in Figure 1. The beaches were chosen to represent different characteristic beach types, including freshwater, marine, estuarine, and riverine. Two contractors, Battelle and Lockheed Martin, were responsible for sample collection; laboratory analyses were performed at sub-contracted laboratories located near each beach.



### Sample Collection

At each site, sampling points were determined based on a nine-point sampling grid. Each grid was made up of three parallel lines 20 meters apart projected perpendicularly from the beach into the water (transects). Transects remained fixed for the study. There were three sampling points on each transect, characterized by water depth. The three sampling points were at ankle-depth, knee-depth, and chest-depth water. Five hundred milliliter water samples were collected in plastic bottles at each sampling point. Samples were thus characterized by transect, depth, date, and time of day. Sampling events were dubbed "visits," which represented each time samples

were scheduled to be collected from the nine sampling points. Each day from July 1 through August 31, samples were collected according to one of the following daily sampling plans:

*Basic Sampling* – Two visits occurred on basic days, one at 9:00 a.m. and one at 2:00 p.m. A single sample was collected at each of the nine sampling points on each visit.

*Hourly Sampling* - Ten visits occurred on hourly days, every hour on the hour from 9:00 a.m. until 6:00 p.m. A single sample was collected at each of the nine sampling points on each visit.

*Replicate Sampling* – Two visits occurred on replicate days, one at 9:00 a.m. and one at 2:00 p.m. On each sampling visit, ten replicate water samples were collected at the central sampling point, and two replicate samples were collected at each of the eight remaining points. The river site (Belle Isle) was an exception with only two samples being collected at the central sampling point.

*Depth Sampling* – Two visits occurred on depth days, one at 9:00 a.m. and one at 2:00 p.m. Samples were collected at each of the nine sampling points, at the standard sampling depth (0.3 meters for knee and chest depth samples). At each knee depth sampling point, an additional sample was collected approximately three inches from the floor. At each chest depth sampling point, two additional samples were collected, one at mid-depth, and one three inches from floor.

Inclement weather, rough water, and other uncontrollable events (such as the Detroit field crew quitting in mid-summer, and samplers being hurt in surfing accidents) affected the number of actual visits that occurred. Table 1 summarizes the types and numbers of visits that occurred at each site, and the approximate number of samples that were collected. The actual total number of samples collected was 11560.

**Table 1. Number of Sampling Visits and Approximate Total Number of Samples Collected at Each Site by Type of Sampling Visit**

	<b>Basic sampling</b>		<b>Hourly</b>		<b>Replicate</b>		<b>Depth</b>	
	<b>Visits</b>	<b>Samples</b>	<b>Visits</b>	<b>Samples</b>	<b>Visits</b>	<b>Samples</b>	<b>Visits</b>	<b>Samples</b>
West Beach	69	610	139	1162	16	416	8	144
Belle Isle	75	671	80	705	16	334	8	138
Wollaston	71	638	138	1242	16	407	8	144
Imperial Beach	68	612	140	1254	16	416	8	144
Miami Beach Park	72	643	140	1257	16	416	8	144

## Field Data Collection

During each sampling visit, the following information was recorded:

- Date and time of the visit
- Air and water temperature
- Wind speed and direction
- Wave height
- Current direction

- Bather density (in the water and on the beach)
- Number of nearby boats
- Number and type of nearby animals
- Observed debris
- Latitude and longitude of each ankle depth sampling point, and the distance from those points to the knee and chest depth sampling points on that transect
- Miscellaneous comments

### Sample Analysis

Freshwater samples (Belle Isle, West Beach) were assayed for *Escherichia coli*, while the marine and estuarine water samples (Wollaston Beach, Miami Beach, Imperial Beach) were analyzed for enterococci. Sample processing (membrane filtration) had to begin within six hours of sample collection, and resulting microbiological plates had to be incubated within eight hours of collection. Generally three sample volumes of each sample were filtered/plated, 1, 10, and 100 mL. After twenty-four hours of incubation, plates were removed and target bacterial colonies were counted. Bacterial counts, sample volumes, and other critical information, such as analysis start time, and incubation start and completion times, were recorded. Each sample also had its pH and turbidity measured, and one sample from each visit (the central sample) was analyzed for total suspended solids.

### Request for a Database

The original statement of work prepared for the EMPACT Beaches Project contained the following language.

*“Data shall be recorded and saved in an electronic spreadsheet (Lotus 123, Excel, or QuattroPro) conforming to the general format as specified in Figure 4 (Note: Figure 4 is not included in this paper). Bacteriological data and beach data records may be contained in separate files or in separate sheets within the same file. All data shall be forwarded to the EPA Project Officer within two (2) days after collection.”*

This was a sketchy description given the volume of data to be collected. Project personnel recognized this, and realized that a complete database was a desired end product. Having spent most of February drafting the QA plan for the project, the EPA QA Manager had spoken extensively with all of the key project personnel, and had developed a good sense of what would be needed from the database. In early April 2000 he sent an email to his local computer support contractors requesting assistance. The request outlined the following desired features and required time frame:

- A “master” database should exist in Cincinnati where the project would be managed.
- Each of the five remote sites should have a sub-database for their site.
- The master database should be able to be updated with weekly submissions from the five sites; ideally such submissions would include only new records (i.e., remote sites shouldn't have to send their entire sub-database each week).

- It would be desirable for remote sites to be able to print forms from the database that could accept hand-entered data.
- User-friendly electronic data entry forms should be developed as part of the database.
- Standard QC sample results for microbiological assays should be reported similarly to regular samples.
- The time frame for completion of a “draft” database was approximately one month, with the possibility of making modifications (such as adding specific QC and locational data fields) up until the presumed start of the project, which at the time was the Memorial Day weekend.

### **Database Design Phase**

The computer support contractor assigned a database developer with close to twenty years of experience to the project. This developer had recently been learning Microsoft Access, having been tasked to convert several legacy databases from outdated software. The QA Manager was also familiar with Access, and it was quickly decided that this would be the application used for the project.

Good databases are effectively representations of reality, and just as a photograph can’t be taken without film, a database can’t be designed without knowledge. Input was needed from the technical staff in order for the developer to understand the physical aspects of the study. Almost daily communications with the QA Manager were the primary conduit for the necessary knowledge to be passed along. The QA Manager and developer conducted numerous “virtual” walk-throughs of sampling visits, picturing how field personnel would likely go through sample and data collection while at the beach. The open and frequent communications between the QA Manager and the developer, combined with input received (and valued) from both federal and contractor technical staff, allowed the developer to design the database. The synergy that developed was notable, and in our minds, unusual. There was no compartmentalization. The right people were involved, at the right time, with the right attitude. In late April, a laboratory workshop was held in Cincinnati. By then, the database was ready to be previewed, and comments from the preview session resulted in further modifications. Though some small changes were made after the field season started, the database was basically complete when the field season arrived.

### **Underlying Principles**

Key to developing a good database was adherence to basic principles of sound database design. Among the rules followed in developing the EMPACT database were the following.

- There would be one official copy of the data. All additions, deletions, or changes in the data would be made to this copy (the master database).
- Entity classes (such as samples, visits, and sites) had separate data tables for each class. For example, sample information such as pH was not in the same table as the visit date, which was in the visit table. Even though a sample was collected on a given date, samples and visits are different entity classes.

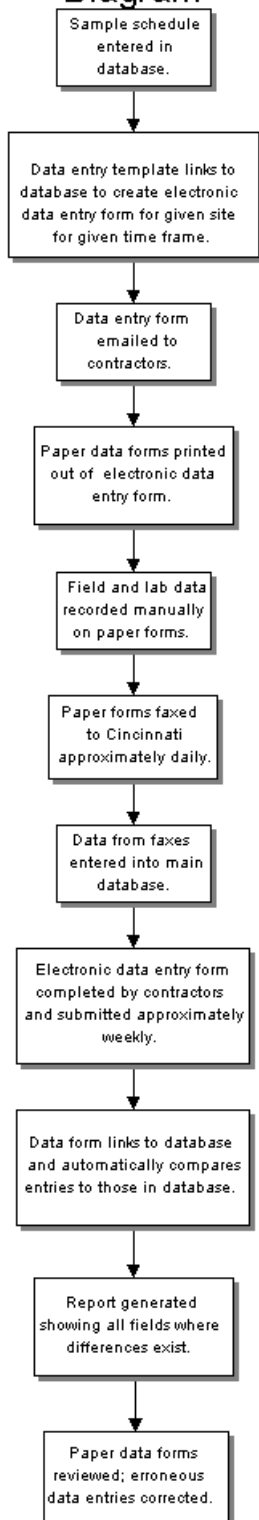
- Every record in data tables described a single, unique instance of an entity class, which meant that every record had unique values in its identifying fields (known as its key). The most important key was the sample ID.
- Each field had a single value. Multiple values were not piggybacked into a single field.
- Tables did not have multiple fields holding multiple values of the same property. For example, weights recorded during replicate suspended solids analyses were not entered in multiple weight fields in the TSS measurements table.
- In instances where an entity class (such as samples and visits) was going to be used at different sites, special effort was made to guarantee that every instance had a unique identifier. A number, ranging from 0001 through 14453, identified every sample bottle. Sample labels with ID numbers were printed in advance in Cincinnati and shipped to each field site.
- Values for identifiers (*e.g.*, sample ID numbers) could not be expressed in more than one way. With sample IDs being a simple number, it was not possible for multiple expressions of the same value. This was ensured in part by having the ID field formatted as a numeric field, and not a character field. Where appropriate, pull down menus were employed to ensure consistent data entry.
- Entity classes were identified with a single field, and this field was only used for identification. More specifically, the field did not contain actual data values. Sample ID numbers are again the best example. They were not some mnemonic containing embedded data. It is not uncommon to see sample IDs that are derived from some combination of date, time, intended analysis, etc. We believe such IDs serve only to complicate matters and often lead to entry errors.

### **Data Management Scheme**

Figure 2 outlines the data management scheme that was used for the study. The database allowed the entire summer's sampling schedule to be entered prior to the field season. A user friendly scheduling form in the database required that a site be picked, dates entered, and visit type (basic, replicate, etc., chosen from a pull down menu) be selected for each date. Pressing a "button" then created the schedule in the database (*i.e.*, a record for each planned visit was created). If the schedule changed (which periodically occurred during the study), one could simply repeat the scheduling process and change the visit type associated with any given date.

The next step in the process involved the use of an electronic template that had been created to allow remote data entry. In this form, a site was selected and a range of dates (usually a week) was chosen, then a button was pressed that linked the form to the master database. The scheduled visits for those dates were then downloaded into the form. After the downloading was complete, the form would be saved under an appropriate name (*e.g.*, 0701.0707.Baltimore would be the electronic data entry form for Baltimore (Miami Beach) for July 1 through July 7). The electronic form was then emailed to the remote contractors. Built into the electronic data entry

## EMPACT Dataflow Diagram



**Figure 2.**

form were printable paper forms that could be used for field and laboratory data collection. The paper forms were designed as much as possible to mirror the pattern of data entry into the electronic forms.

At the remote sites, the contractors would collect field and laboratory data on the supplied paper forms. As soon as microbiological analyses were complete and recorded on the forms, they would fax the forms to Cincinnati. This meant data was arriving daily. The faxes were organized by date and visit in ring binders for each site. Copies of the faxes were passed to data entry subcontractors (in Cincinnati), who would enter the data into the master database.

Upon completing all the analyses and data entry related to the current electronic data entry form (e.g., 0701.0707.Baltimore), the remote (field site) contractors would email it to Cincinnati. The electronic data entry form had a “button” on it that allowed its contents to be compared to all of the entries in the master database for the same visits. If any differences were detected, buttons would appear that would bring up reports showing where the differences were. The paper forms would then be reviewed, and corrections would be made to the master database and/or the submitted electronic form, depending on where the errors were. (In some cases, the error correction process lead to detection of errors on the paper forms, which were also corrected where possible). After error correction was completed, the comparison routine was rerun to verify the corrections. Paper records were maintained showing the corrections that were made.

Data entry proved to be quite time consuming, however by December of 2000, all data was entered and verified as matching that on the paper forms. Given the volume of information collected, we view this as a significant achievement.

## Conclusion

The data management scheme employed for the EMPACT Beaches Project was a success. A vast quantity of information was generated and accurately captured in a database that will be made public. The main reason for the success of the project was that data management was planned for in advance, as part of the QA planning process. The right people were involved, and their input was sought and acted on. A more detailed analysis of the costs and benefits of the employed process is merited, however the potential use of the established framework on future projects supports the idea that the return on investment could prove significant.

## **The Use of Measurement Uncertainty and Statistics in ORD Research Products**

Paul W. Groff, U.S. EPA

*Researchers in the Office of Research and Development (ORD) use statistics to evaluate data and draw conclusions. Often these data are obtained using data acquisition systems (DAS) that can generate a large number of samples. Many of the statistical tools have assumptions, such as sample independence and distribution type. These tools can allow the researcher to develop confidence intervals for data or identify one group of data to be different than another in a parametric test. The reporting of the data and the conclusions can be misleading if the wrong tool is used. This paper presents some statistics terms such as measurement uncertainty, mean, standard error of the mean, and standard deviation and how they have been used in reporting results of some ORD research. One of the main themes of EPA Order 5360.1 is that information produced by EPA must be of known and adequate quality. Measurement uncertainty is the internationally accepted qualifier for measurements. Some measurements have straightforward uncertainty calculations, others have extremely difficult calculations, and this is demonstrated with examples of ORD measurement uncertainty calculations.*

## **The Use of Sensitivity as a Data Quality Indicator: The Office of Water's Reassessment of Detection and Quantitation Concepts**

William Telliard and Marion Kelly, U.S. EPA, Engineering and Analysis Division  
Harry B. McCarty, Lynn S. Riddick, and Ken Miller  
DynCorp Systems and Solutions

*On June 8, 1999, EPA published a final rule adding EPA Method 1631B, for the analysis of mercury at low levels, to the list of monitoring methods approved under Section 304(h) of the Clean Water Act. Following promulgation, an industry group filed a lawsuit challenging promulgation of the method. The challenge addressed specific aspects of EPA Method 1631B as well as the general procedures used to establish the method detection limit (MDL) and the minimum level of quantitation (ML) specified in the method. On October 19, 2000, EPA entered into a settlement agreement that requires that EPA complete an assessment of procedures for determining the detection and quantitation limits in Clean Water Act Programs, and publish the results in the Federal Register by February 28, 2003.*

*In the context of data quality indicators, the term "sensitivity" has been used to refer to the capability of a method or instrument to discriminate between small differences in analyte concentration. Sensitivity is a function of both the precision of the measurement technique and the slope of the calibration.*

*A detection limit is the lowest concentration or amount of a substance that allows for differentiation between a sample that contains the substance and one that does not. A quantitation limit is the lowest concentration or amount of a substance that can be measured with some stated level of confidence. To date, there is no general consensus among various government agencies, method developers, or scientific organizations on the most appropriate approach to one define detection and quantitation. EPA estimates that more than 50 different terms have been used in published analytical test methods to describe detection and quantitation capabilities, and in many instances, the same term is used by different organizations to mean different things.*

*Nearly all of the detection and quantitation concepts advanced to date fall into one of two main categories: 1) those that assume measurement error is constant or effectively constant in the low concentration range and are based on the error observed in replicate measurements made at a single low concentration, and 2) those that assume measurement error varies as a function of concentration and are based on the error observed in replicate measurements gathered across the measurement range. Examples of the first category include the concepts first advanced by Lloyd Currie (1968) and later adopted in various forms by the American Chemical Society (ACS), the International Standards Organization (ISO), the International Union of Pure and Applied Chemistry (IUPAC), and EPA. Examples of the second category include the concepts first advanced by Hubaux and Vos (1970) and later adopted by ASTM-International.*

*The controversy concerning detection and quantitation limits has been exacerbated by frequent confusion of detection and quantitation limits with compliance and reporting limits. Recent efforts to describe the use of sensitivity as a data quality*

*indicator have increased interest in the application of detection and quantitation limits. This paper presents the results of EPA's recent reassessment of detection and quantitation concepts employed under the Clean Water Act and discusses the ramifications regarding the evaluation of sensitivity.*